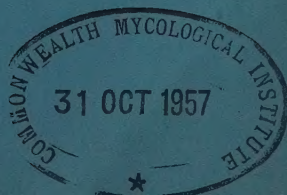# ENDEAVOUR

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ENDEAVOUR

The British quarterly scientific journal ENDEAVOUR was first published, by Imperial Chemical Industries Limited, in January 1942. Its purpose is to provide scientists, especially those overseas, with news of the progress of the sciences. While emphasis is laid upon British work, occasional articles from overseas contributors are included and impartial reference is made to the world's scientific literature. To make the journal truly international in character it is published in five separate editions—English, French, German, Italian, and Spanish.

No charge is made for ENDEAVOUR. It is distributed to senior scientists, scientific institutions, and libraries throughout the world, the guiding principle being that of helping scientists overseas to maintain those contacts which their British colleagues have always so much valued. Within these limits the Editors are at all times glad to consider the addition of new names to the mailing list.

The drawing on the cover is of the bark Endeavour, *which, commanded by Captain James Cook and carrying a number of scientific workers, was sent out by the British Admiralty in 1768 to chart the South Pacific Ocean and observe the transit of Venus*

ENDEAVOUR

A quarterly review designed to record the
progress of the sciences in the service
of mankind

CONTENTS

Réaumur, a forgotten technologist

René-Antoine Ferchault de Réaumur was born on 28th February 1683 and died just two centuries ago, on 18th October 1757, after nearly fifty years of very active membership of the Paris Academy of Sciences. He was elected to the Academy at the early age of twenty-five; he contributed seventy-five original memoirs to its proceedings, almost equally divided between the physical and the biological sciences; he was director twelve times, on the first occasion when he was only thirty-one, and deputy-director nine times. The breadth of his knowledge so impressed those who knew him that he was described as 'the Pliny of the eighteenth century'. Despite this, the general public even in his own country are reminded of him only by a thermometer that bears his name—but has no resemblance to the instrument that he devised—and by a station on the Paris 'Métro'.

Réaumur first studied law but preferred mathematics and physics, and it was as a mathematician and 'pupil' of the geometer Varignon that he entered the Academy of Sciences. After submitting a few mathematical papers, he turned to natural history and to the useful arts, or what we now call technology. In natural history he made one discovery after another in a remarkable series of experiments and observations, which it is impossible to recall here even in the briefest terms. Mention must, however, be made of his great *Mémoires pour servir à l'histoire des insectes*, published in six quarto volumes in Paris from 1734 to 1742. This was a work of about 4000 pages with over 250 plates, carrying in all about 5000 illustrations. By this monumental study Réaumur became one of the founders of entomology. Publication was incomplete when he died and a seventh volume has recently appeared, two centuries after the sixth, while material for an eighth is available.

In 1711 Réaumur was promoted in the Academy to *pensionnaire mécanicien*: the *pensionnaire* indicates that he received a small salary and the *mécanicien* is perhaps best rendered in English as engineer or even as technologist. By this promotion his interest in the useful arts was recognized, and he was placed in charge of the Academy's projected compilation of a series of volumes on the various industries and trades. This was the famous *Descriptions des Arts et Métiers*, which appeared in 27 folio volumes from 1761 onwards, all after Réaumur's death.

His interest in technology was remarkable. He reported to the Academy on the manufacture of mirrors, the working of slate, making artificial pearls, the gilding of leather, mining for iron, the drawing of gold wire, the properties of paper, alluvial gold in French rivers, and many other topics. In 1722 he made what is probably his most important contribution to technology in his *L'Art de convertir le Fer forgé en Acier*, etc., which has lately been translated into English. It is enough to emphasize here the experimental nature of Réaumur's researches on iron and steel: this work was essentially a technical research, and it was intended to encourage the practical application of the results that it announced. It led to the introduction into France of the manufacture of steel. For this important contribution to French industry Réaumur received from the Duke of Orléans, then Regent of France as Louis xv was still a minor, an annual pension of 12 000 livres. The terms of this grant were modified, at Réaumur's request, so that after his death the allowance might be perpetuated to the Academy for the further promotion of experimental studies on the improvement of the useful arts.

A few years previously, in 1715, Réaumur had reported to the Academy on the neglected turquoise-mines in Languedoc. He showed that the native gemstones were as good as those brought from Persia, and he carried out experiments that led him to conclude that the turquoise consisted of fossilized bones coloured by fusion with some metallic substance. This was a creditable conclusion in the light of the chemical knowledge of that time, and indeed one not without a germ of truth, for we now know this material to be a copper aluminium phosphate.

After his work on iron and steel, Réaumur's attention was turned in 1725 to the manufacture of another product that was imported into France from Germany, namely tinplate. Again he proceeded to experiment; as with steel, the product was known but the process of making it was kept secret, or at least as secret as trade-processes could be kept. Réaumur found that one of the important stages in the plating process was the removal of scale from the iron to give a clean surface for tinning. By experiment he discovered that vinegar was both the most satisfactory and the cheapest agent for this. Another industry was thus introduced into France.

In 1727–29 he made similar researches on

porcelain, comparing that from China and Japan with that produced in France and Germany. He noted that oriental porcelain had a solid compact texture, and that the European imitations of it were porous. He heated all three and found that, while that from China was unaffected, the French and the German products both vitrified. These results led him to conclude that European porcelain contained two vitrifiable substances, and that the Japanese product was made from one vitrifiable ingredient and another that was non-vitrifiable, the former on fusion enveloping the latter to give a semi-transparent product. This work was subsequently extended by his successors, more particularly by Macquer (ENDEAVOUR, 16, 133, 1957), a director of the Royal Porcelain Factory at Sèvres.

Besides these studies, Réaumur compiled a volume on the manufacture of anchors and another on the making of pins, as well as a new edition of the book on making cast iron malleable. He showed how to preserve eggs in a state of freshness for long periods: he found that it was necessary to seal the pores of the shell and that this could be done by means of a coating of varnish or grease. His classic studies on the artificial incubation of eggs appeared in a well-illustrated two-volume work in 1749 and in a later abridged edition, as well as in translations.

Enough has been said here to indicate Réaumur's deep interest and active concern in all practical applications of scientific knowledge and discovery, and in the improvement of the useful arts through a scientific understanding of the processes involved. All work of this kind that he embarked upon was inspired by the belief that the scientific and the useful were indissolubly connected.

This belief is revealed in a most striking manner in a memorandum ascribed to Réaumur and quoted by Maindron, the historian of the Academy of Sciences. Written between 1716 and 1727, this document emphasizes the services that the Academy could render to France if it were provided with such financial support as would, in Réaumur's view, prove trivial in comparison with the valuable results that would follow. The memorandum criticized the wisdom of relying for scientific progress on the spare-time studies and experiments of men engaged in other pursuits for the greatest part of every day. It pointed to the usefulness of astronomy in navigation, in cartography, and in the study of tides. It stressed the importance of mechanics in all matters related to machines, and the practical value of chemistry, botany, and anatomy were made equally clear. The importance of mechanics was particularly emphasized, and this science was ranked among those most useful to a nation. As for the *mécaniciens* themselves, Réaumur explained that those whom he had in mind were not the ordinary craftsmen with a knowledge of the motive powers and able to give an opinion about new machines that might be proposed; he was thinking rather of men thoroughly instructed in all the arts, aware of their defects and intent on their improvement, and eager to introduce into France suitable new industries that had already been successfully established in other countries. He proposed the creation of various salaried appointments, within their special fields of interest, for members of the Academy, so that their livelihood would be secured. He recommended that a collection of all native raw materials should be established and that a large laboratory should be set up for the use of the Academy, every member of which should have a special annual task allotted to him as one of his studies.

Réaumur was truly Baconian in seeing no limit to the useful things that might be discovered by such a reorganization and endowment. He was most modern in his fear of the perils of inflation, pointing out that the success of such a scheme would depend, not on the granting of sums of money that might be affected by various changes, but by such solid endowments in land as were possessed by the universities of Oxford and Cambridge. He considered that a single discovery might well repay the whole cost. He concluded the memorandum by saying that it was a mere sketch of the advantages that might be derived from the work of the Academy for the furtherance of the wealth and glory of France, as had been intended by Colbert when the Academy was first established. Written perhaps about 1720, the memorandum reveals the far-sighted vision of one who saw science almost with the eyes of Francis Bacon, but with far greater knowledge and understanding, and one who was among the first to realize that it is only from the finest theory that the finest practice is born.

Nuclear magnetic resonance

R. E. RICHARDS

Nuclear resonance spectra in bulk matter were first observed in 1945. In the relatively short time that has since elapsed, nuclear resonance spectra have been used to solve an extraordinary range of problems in physics and chemistry: from the extremely accurate determination of nuclear moments to the estimation of moisture in solids, from the study of minute defects in crystal lattices to the elucidation of the structures of complicated organic molecules.

GENERAL PRINCIPLES

When atomic nuclei are placed in a constant magnetic field of high intensity and subjected at the same time to a radio-frequency alternating field, a transfer of energy takes place between the high-frequency field and the nucleus. This phenomenon is known as nuclear magnetic resonance. Spectra due to nuclear magnetic resonance result from many atomic nuclei having 'spin' angular momentum. This property of spin was first ascribed to the nucleus by Pauli in 1924 to account for certain aspects of atomic spectra, and nuclear spin has since become an important concept in the explanation of various other phenomena such as the existence of ortho and para states of certain molecules like hydrogen. Not until 1945, however, were nuclear magnetic resonance spectra observed in bulk material, and then almost simultaneously by E. M. Purcell, H. C. Torrey, and R. V. Pound [1], and by F. Bloch, W. W. Hansen, and M. E. Packard [2].

The idea of spin of the electron is now a familiar one. Just as we characterize the spin of the electron by a quantum number, $s = \frac{1}{2}$, so the spin angular momentum of a nucleus is characterized by another quantum number, usually symbolized as I. For nuclei, $I = n/2$, where n is zero or integral; for a given nucleus the value of n must be found experimentally.

Since the nucleus is positively charged, there is associated with its spin a circulation of electric charge. Just as the circulation of electric charge gives rise to a magnetic moment when a current flows through a coil of wire, so the circulation of charge associated with the spin of the nucleus causes it to possess a magnetic moment. The nucleus may therefore be regarded as a spinning particle with a weak magnetic moment directed along its axis of spin. This moment can be expressed as

$$g\beta[I(I + 1)]^{\frac{1}{2}}$$

where β is a unit of magnetic moment called the nuclear magneton, and g is the 'nuclear g factor' which must be found by experiment.

If a nucleus is placed in a uniform magnetic field, H_0, it experiences a torque which tends to orient it so that its North-seeking pole points towards the North pole of the magnet generating the field, just as a compass needle is oriented by the Earth's magnetic field to point North and South. Unlike a compass needle, however, the nucleus does not assume the most stable orientation in the magnetic field more or less immediately, but precesses about the applied field. This motion arises from the interaction of the angular momentum of the nucleus with the torque exerted on it by the magnetic field; it is analogous to the precession of a gyroscope spinning in the Earth's gravitational field (figure 1).

The potential energy of the nuclear magnet in the magnetic field H_0 clearly depends on its orientation with respect to the field, because the torque exerted by the magnetic field always tries to turn the nucleus towards its most stable position, in which the component of the nuclear moment along H_0 is a maximum. The quantum theory requires that this energy shall be quantized in such a way that the component of magnetic moment in the direction of H_0 is $mg\beta$, where $m = I, I - 1, I - 2, \ldots, 0, -1, -2, \ldots, -I$. The potential energy of the nucleus in these levels can therefore be expressed as

$$U(m) = -H_0 mg\beta \qquad \ldots . (1)$$

Each energy level corresponds to a different orientation of the nuclear magnet with respect to the field H_0. The number of allowed levels is clearly $2I + 1$, and in each of these levels the nucleus precesses about the direction of H_0, but maintains its correct orientation in the field. Figure 2 shows the possible energy levels in the magnetic field for the simple case of nuclei having spin quantum number $I = \frac{1}{2}$ and $I = 1$. The maximum allowed
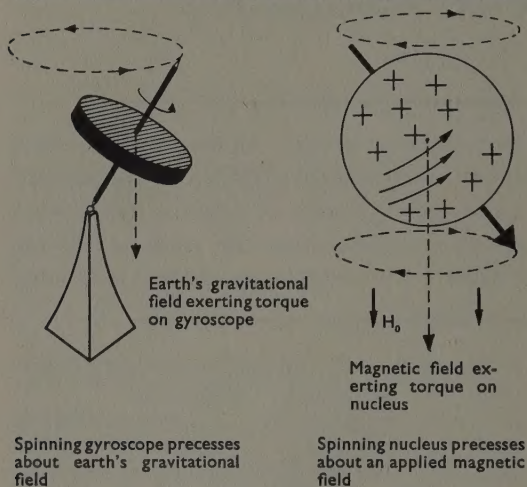
Earth's gravitational field exerting torque on gyroscope

Magnetic field exerting torque on nucleus

Spinning gyroscope precesses about earth's gravitational field

Spinning nucleus precesses about an applied magnetic field

FIGURE I – *Precession in gravitational and magnetic fields.*

component of the magnetic moment along the field, when $m = I$, is $Ig\beta$, and it is this quantity which is usually referred to as 'the magnetic moment', μ, of the nucleus. From (1) it follows that the energy difference between two adjacent levels, m and $m + 1$, is given by

$$\Delta U(m \to m + 1) = U(m) - U(m + 1)$$
$$= H_0 g\beta(m + 1 - m) = H_0 g\beta = \mu H_0/I \ldots . (2)$$

If a system of nuclei in a magnetic field is exposed to radiation of frequency ν_0, such that the energy of a quantum of the radiation, $h\nu_0$, is exactly equal to the energy difference between two adjacent nuclear energy levels $(H_0 g\beta)$, then energy transitions may occur in which the nuclei are as it were flipped back and forth from one allowed orientation to another.

A quantum of energy is equally likely to tip a nucleus in either direction, so there is a net absorption of energy from the radiation only when the number of nuclei in one energy level exceeds the number in another. Such an excess would occur if the nuclei were in thermal equilibrium with their surroundings, and therefore populated their energy levels according to a Boltzmann distribution. In these circumstances a nuclear magnetic resonance spectrum is observed, the lines in the spectrum corresponding to the energies required to flip the nuclei among their allowed orientations in the magnetic field. Since the energy levels are equally spaced, only one line is observed, at a frequency corresponding to the constant difference, $g\beta H_0 = \mu H_0/I$, between the energy levels.

The radiation required for these experiments

lies in the radio-frequency region. For example, for protons in a field of 10 000 gauss, radiation of frequency about 42·6 Mc/s is required. As there is a linear relation between the resonance frequency ν_0 and the magnetic field H_0, nuclear magnetic resonance spectra can be expressed equally well as intensity of absorption plotted against frequency, at fixed field H_0, or against magnetic field at fixed frequency ν_0. One scale is readily converted to the other by the numerical factor relating H_0 and ν_0.

MEASUREMENT OF NUCLEAR MOMENTS

The relationship between H_0, ν_0, and μ for a nucleus provides a method of measuring nuclear moments, and this was first used by I. I. Rabi and his colleagues [3] in studying nuclear resonance in the nuclei of atomic and molecular beams. The direct observation of such spectra in bulk matter provides an accurate method of measuring ν_0 in a given field H_0, and extensive measurements of nuclear moments have been compiled [4]. The accuracy of the measurements is limited by the accuracy of the determination of the frequency at the centre of the line and of the magnetic field measurement. The accuracy of the frequency measurement is limited by the line width, which is extremely small in liquids; in solids, however, the lines are often broad and unsuitable for measurement. An important limitation is connected with the magnetic field at the nucleus; this is not identical with the applied magnetic field because of the influence of the extranuclear electrons. This effect can lead to errors in the measurement of nuclear moments ranging from a few parts per million to one part in a thousand, but the study of the effect itself in different molecules leads to other important inferences. The spectra are also often
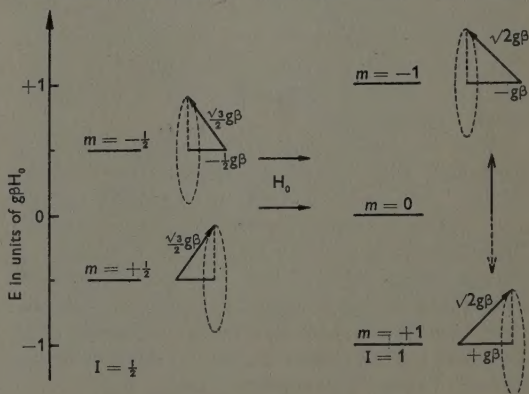

FIGURE 2 – *Energy levels in magnetic field for nuclei having $I = \frac{1}{2}$ and $I = 1$.*

complicated by interactions between the nuclei themselves, or between the nuclei and the molecular electrons, and we shall later consider how these interactions can yield useful information. Before doing so, however, something must be said of the general nature of the apparatus used.

APPARATUS

The apparatus for nuclear magnetic resonance experiments is relatively simple. A large magnet is required to provide the main field H_0, and electronic equipment to generate the radio-frequency radiation and to measure its absorption by the sample. The radio-frequency equipment need not be very complicated, and its construction involves only well known principles of radio- and audio-frequency techniques. The magnet may be either electrically energized or a permanent magnet; each has special merits for particular applications. The magnetic field generally used is in the range 3000–12 000 gauss; it is an advantage to work at the highest field strength that can be obtained. For the study of broad lines, a small magnet with pole faces of about 13 cm diameter and a gap of about 5 cm is convenient. To measure the very sharp lines from liquids, the magnet must provide a field that is stable and homogeneous over the sample by an amount less than the line-width. For 'high resolution' measurements on liquids, this means that the homogeneity and stability of the field must be about 1 part in 10^8, and this formidable specification can at present be met only by rather large and elaborate magnets.

STRUCTURE OF SOLIDS AND INTERNUCLEAR DISTANCES

Because of its magnetic moment μ, a hydrogen nucleus ($I = \frac{1}{2}$) fixed rigidly in a crystal generates a weak local magnetic field H_{loc}. A second nucleus, near by, therefore experiences a total field ($H_0 \pm H_{loc}$), the sign depending on the particular orientation in the applied field adopted by the first nucleus. H_{loc} is proportional to μ/d^3, where d is the internuclear distance, because the magnetic field generated at a distance D from a point dipole is proportional to μ/D^3.

A solid containing pairs of hydrogen nuclei, such as a salt hydrate, will therefore give a proton resonance spectrum in the form of a doublet; the two components correspond to the two effective fields, ($H_0 + H_{loc}$) and ($H_0 - H_{loc}$), which any individual nucleus can experience through magnetic interaction with its neighbour.

It can be shown that triangular configurations of nuclei in a solid give absorption curves with three peaks [5], and tetrahedral arrangements give absorption curves with rather flat tops [6]. The shape of the curve can therefore be used to identify the configuration of nuclei in simple cases; moreover, as the widths are proportional to $1/d^3$, the internuclear distances can also be measured. This method is particularly useful for studying hydrogen atoms, which are so difficult to locate accurately by other methods [7].

The use of the method may be illustrated by studies on boron trifluoride dihydrate [8]. In the liquid state this substance has been shown by Raman spectra and conductivity measurements to be ionized, to the extent of about 20 per cent, according to the equation

$$BF_3.2H_2O \rightleftharpoons [BF_3OH]^- + H_3O^+$$
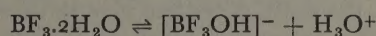
In the crystalline hydrate the structure must be either entirely non-ionized or completely ionic. In the former case a proton resonance would find expression in a broad doublet, due to the pairs of protons in the water molecules; in the latter case the proton resonance would be wider and have three maxima, of which the central one would be the more intense because of the narrow component of the relatively isolated hydrogen of the $[BF_3OH]^-$ ion. It was in fact found that slowly crystallized boron trifluoride dihydrate gives a doublet proton resonance at 90° K, showing that it has passed completely into the non-ionized condition.

This behaviour is in contrast with nitric acid monohydrate, which in the liquid state is ionized to about the same extent as boron trifluoride dihydrate:

$$HNO_3.H_2O \rightleftharpoons H_3O^+ + NO_3^-$$
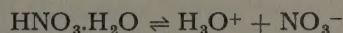
When this substance is crystallized, it becomes completely ionic [9] and the proton resonance has three maxima.

With both $BF_3.2H_2O$ and $HNO_3.H_2O$ it was found that rapid cooling of the liquid would produce a glass which showed proton resonance spectra consistent with the presence of both ionized and non-ionized molecules. If it is possible to grow large single-crystals, more can be learnt, such as the orientation of the molecules with respect to the crystal axes.

In crystals which contain more complicated groups of nuclei, the absorption lines usually coalesce to give one undefined curve. J. H. Van Vleck [10] has shown that the mean square width, or second moment, of the absorption curve is

related to the sum of the inverse sixth powers of the internuclear distances in the crystal. It is often possible to use this relationship to locate the hydrogen atoms in a crystal when the positions of the other atoms have been found by X-ray methods, or when there is a high degree of symmetry. Measurements of bond lengths to hydrogen have been made by this method on the ions NH_4^+ [6], PH_4^+ [11], BH_4^- [12], and NH_2^- [13]. The hydrogen atom has been located in the hydrogen bonds formed in the HF_2^- ion and in hydrazine fluoride. In the former [14] the hydrogen atom is found to be centrally placed between the two fluorine atoms; in the latter, however, the N–H distance is 1·075 Å, while the H–F distance is 1·542 Å [15].

When resonances of nuclei for which $I > \frac{1}{2}$ are studied, the width of the line may be determined by another interaction much more potent than that considered above. Nuclei with spin quantum numbers greater than one-half usually possess an electric quadrupole moment as well as a magnetic dipole moment. The electric quadrupole moment arises from aspherical distribution of the positive charge over the nucleus; the charge may be distributed over a prolate or an oblate ellipsoid, and which of these obtains determines the sign of the electric quadrupole moment.

In a uniform electric field the magnitude of the quadrupole moment is independent of its orientation, but if the electric field has a gradient—which might arise, for example, from an unsymmetrical arrangement of other atoms in the molecule—then the energy of the nucleus will be lower in certain orientations than in others. For example, a nucleus with a sausage-shaped distribution of positive charge will prefer to orient itself in the region of lowest positive potential in a non-uniform electric field. The energy of the nucleus due to its angular orientation has the form:

Quadrupole moment × field gradient
$$\times\ [3m^2 - I(I + 1)]$$

and has to be added to or subtracted from the magnetic energy levels according to the sign of the term $[3m^2 - I(I + 1)]$. Some of the magnetic energy levels are therefore raised and some lowered, since $m = I, I - 1, \ldots 0, -1, \ldots -I$. This is illustrated in figure 3, which relates to a nucleus for which $I = 3/2$. The levels for which $m = \pm 3/2$ are raised in energy by the electric quadrupole interaction, and those for which $m = \pm \frac{1}{2}$ are lowered in energy. The nuclear energy levels characterized by the different values of m are now no longer equally spaced, and instead of one

observed absorption line there are several—in this case three. From measurement of the separation between the nuclear resonance lines this quadrupole interaction can be calculated, as a product of the electric field gradient at the nucleus and the nuclear electric quadrupole moment. If one of these parameters is known, the other can be evaluated. Unfortunately nuclear quadrupole moments are not very accurately known, but in some cases measurements of these effects in single-crystals can give extremely detailed information about the crystal structure [16, 17].

The quadrupole interaction energy is zero in perfect cubic crystals because there is no electric-field gradient at the nucleus. Small imperfections in the crystals, or even mechanical strains, can destroy this electric field symmetry, and the broadening or splitting of the nuclear resonance lines can provide an extremely sensitive measure of such an effect [16].

MOLECULAR MOTION IN SOLIDS

The widths and shapes of the absorption lines in the nuclear magnetic resonance spectra of solids are often found to depend on temperature; the absorption lines become narrower rather suddenly as the temperature is raised. The local magnetic fields generated by neighbouring nuclei are evidently being reduced as the temperature is raised. The usual mechanism by which this is effected is molecular motion in the solid, which more or less evens out the interactions. The molecular motion usually consists in hindered reorientation among a number of stable positions, and from the shape and width of the line at high temperatures the nature
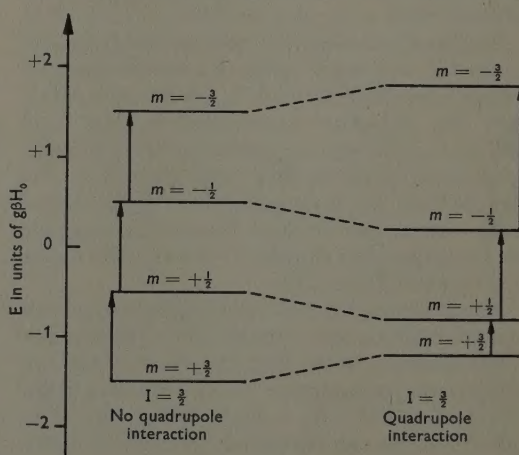

FIGURE 3 – *Energy of nucleus in non-uniform electric field, with and without quadrupole interaction.*

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ALPHABETICAL KEY

of the motion can be discovered. For example, it has been shown [18] that at 93° K the CH_3 group of acetonitrile undergoes hindered motion in the solid about the C–C axis, and that in hydrazine sulphate the $N_2H_6^{++}$ ion reorients itself about the N–N axis at room temperature [19]. Motion taking place during self-diffusion can also bring about narrowing of nuclear resonance lines.

Further information about molecular motion can be derived from a study of the so-called 'spin lattice relaxation time', T_1, of the nuclei. This defines the time required for a nucleus to exchange a quantum of energy with its immediate surroundings. A nucleus having spin quantum number $I = \frac{1}{2}$, occupying one of its allowed energy levels in a magnetic field, enters into no interaction that can change its orientation within the molecule or crystal in which it is situated, except that resulting from its own magnetic moment. Its energy level, or orientation, can therefore be changed only by the influence of a magnetic field oscillating at a frequency near the resonance frequency. It has been shown that the coefficient of spontaneous emission by a nucleus in an upper energy level is quite minute, but it is found experimentally that the lifetimes of nuclei in a given level vary enormously, from times of the order of 10^{-4} seconds to many hours; these lifetimes are expressed in terms of T_1. If the molecules in a solid are jumping back and forth among a number of allowed rotational positions, then the local fields generated by the nuclei of a molecule, and experienced also by neighbouring nuclei, will fluctuate in intensity. There will usually be a range of frequencies of field fluctuations, with a maximum at some particular frequency. The component of this range of frequencies that is near the resonance frequency of neighbouring nuclei will be able to induce transitions in them; energy can thus be exchanged between the nuclear magnetic energy levels and the molecular motion. This process is the more effective the more intense are the local field fluctuations near the resonant frequency.

The vibrational frequency at which molecular reorientation occurs in a solid usually rises with temperature, so that the region of maximum intensity of the local field fluctuations also rises in frequency as the temperature is raised. Thus the relaxation of the nuclei by this mechanism is most effective when the temperature of the crystal is such that the maximum intensity of the local field fluctuations corresponds to the resonance frequency of the nuclei; under these conditions, a short relaxation time, T_1, is observed. If the temperature is lowered from this point, the local field fluctuations slow down and their maximum intensity shifts to lower frequencies, away from the resonance frequency. Relaxation of the nuclei becomes less effective, and in consequence T_1 rises. Similarly, at higher temperatures the maximum intensity in the spectrum of local field-fluctuations due to molecular motion shifts to frequencies higher than the resonance frequency, relaxation again becomes less effective, and again T_1 rises. A graph of T_1 against temperature for these solids therefore shows a minimum T_1 at a temperature at which the spectrum of frequencies of molecular motion is distributed with maximum intensity near the nuclear resonance frequency.

A study of the variation of T_1 with temperature therefore permits a calculation of the way in which the frequency of molecular motion varies with temperature. If the molecular motion is assumed to be hindered by a potential barrier of height V_0, it would be expected that the number of molecules able to surmount the barrier would be proportional to $\exp(-V_0/RT)$, and so from the variation of frequency of reorientation with temperature it is possible to calculate the height of the barrier hindering the motion. It has been shown [20], from the observed change in T_1 with temperature, that in crystalline benzene the molecules undergo hindered reorientation about their hexad axes. The frequency of reorientation of the molecules varies logarithmically with temperature from 10^4/sec at 85° K to about 10^{11}/sec near the melting point, corresponding to a potential barrier of $3 \cdot 7 \pm 0 \cdot 2$ kcal/mole.

Self-diffusion also provides a mechanism for narrowing the absorption line and reducing T_1. Its effect in solid cyclohexane is significant [21]; in the alkali metals [22] large changes in line-width with temperature can be interpreted in this way.

LINE WIDTHS IN LIQUIDS

When a solid is melted or dissolved in a solvent, the molecular motion in the liquid is so vigorous as to even out completely all the broadening interactions so far discussed, and very narrow absorption lines may be obtained. Line-widths in liquids vary from about 10^{-4} gauss to many gauss, depending on circumstances.

A system containing a liquid and a solid phase will give a nuclear resonance spectrum which is a superposition of a narrow and a broad line. It is particularly easy to measure the intensity of the narrow component of the spectrum, which is due to the liquid, and this is a measure of the number

of nuclei in the liquid phase. It is therefore easy to estimate quantitatively the liquid component of a solid-liquid mixture, such as the content of moisture in materials.

Since the local magnetic fields generated by the nuclei are averaged to zero by the random molecular motion in liquids, these cannot contribute to the line-width, which is now dominated by relaxation processes. If T_1 is regarded as a measure of the lifetime of a nucleus in a given energy level, then the Heisenberg uncertainty principle predicts a broadening of the energy level approximately in accordance with the equation

$$\Delta E \times T_1 = h\Delta\nu \times T_1 \simeq h/2\pi$$

This equation is not strictly accurate because the energy level is also broadened by other factors, but it gives the correct order of magnitude. In most organic liquids the value of T_1 for the protons is a few seconds, so that line-widths equivalent to about 2×10^{-4} gauss are observed. In viscous liquids, such as glycerine, the spectrum of local magnetic-field fluctuations due to the Brownian motion of the nuclei in the molecules has its region of maximum intensity at higher frequencies than in mobile liquids; the components of the spectrum near the nuclear resonance frequency are more intense for viscous liquids than for mobile liquids. It is therefore found that viscous liquids have short nuclear relaxation times and the proton resonance lines are correspondingly broadened. If the nucleus possesses an electric quadrupole moment, the nuclear relaxation time may be very short. If an atom in a molecule experiences at its nucleus an electric-field gradient resulting from the arrangement of the other atoms about it, this can produce strong electric quadrupole coupling with the nucleus of the central atom. As the molecule tumbles over in the liquid, the quadrupole interaction drags the nucleus over with the molecule and re-orientates it in the magnetic field in another allowed position. This effect can very greatly shorten the relaxation time and lead to broad nuclear resonance lines. When a change occurs in the molecule that increases the symmetry of the environment of the nucleus, the quadrupole interaction is reduced, T_1 becomes longer and the nuclear resonance line narrower. For example, the chlorine resonance line of the symmetrical ClO_4^- ion in aqueous solution is much narrower than the chlorine resonance line of the ClO_3^- ion [23]. This phenomenon has not yet been investigated extensively, but it promises to be a useful method of studying the structures of liquids and solutions.

CHEMICAL SHIFTS

The frequency at which a nuclear resonance line occurs is governed by the equation $h\nu_0 = \mu H_0/I$. Here H_0 is the magnetic field actually experienced by the nucleus, and, as has been indicated, this is not quite identical with the field applied to the sample by the magnet (H_{appl}). Two factors modify the applied field to give the resultant field H_0; both are effects induced in the molecular electron clouds by the applied magnetic field. They are therefore proportional to the applied field, and

$$H_0 = H_{appl}(1 - a + b)$$

The first term, a, is negative, and arises from the diamagnetism which is induced by H_{appl} in the molecular electrons. It is a property of all bulk matter that when it is placed in a magnetic field, circulating currents are induced in the electron clouds and generate a weak magnetic moment to oppose the applied field. This effect therefore reduces the magnetic field at the nucleus, and it is for this reason that we assign to a a negative sign. The second effect induced by the magnetic field is quantum-mechanical in origin; it can be regarded as a weak uncoupling of the valence electrons, which are normally perfectly paired. When the electrons are paired, their spins are opposed and in consequence the magnetic moments associated with them cancel one another. The applied magnetic field induces a slight deviation from this perfect pairing of the electron spins. A resultant paramagnetic moment is induced, which increases the effective field at the nucleus, so we assign a positive sign to b, which is often called the 'temperature-independent paramagnetism'. Both effects are induced by the field and proportional to it, and it is unfortunately not possible to separate them experimentally. Their combined effect may be written

$$H_0 = H_{appl}(1 - a + b) = H_{appl}(1 - c)$$

and it is found experimentally that the fraction c varies critically with the particular electron distribution or chemical environment of the nucleus.

It therefore follows from the above that, in a given applied magnetic field, the nuclear resonance line will occur at a frequency which varies with c and hence with the chemical environment of the nucleus. Alcohol, for example, shows three proton resonance lines having intensities in the ratio 3 : 2 : 1. The three lines arise from the protons in the methyl, methylene, and hydroxyl groups respectively; their intensities are proportional to the number of protons in each group. The characteristic positions of the resonance lines are referred
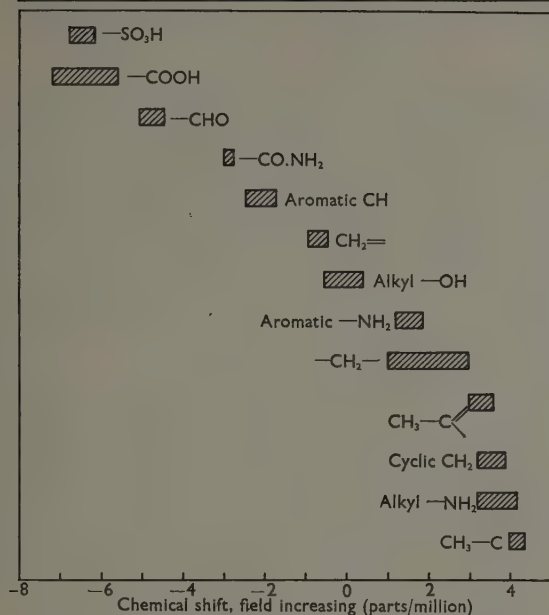
FIGURE 4 – *Chemical shifts in relation to functional groups.*

to in terms of 'chemical shifts', which are usually expressed as a fraction of the field by which the resonance is shifted from some arbitrary standard. The chemical shifts of proton resonance lines can be related to the functional groups in which the protons occur; figure 4 shows a few examples [24]. From the nuclear magnetic resonance spectrum of an unknown substance certain groupings can be identified, and often their relative numbers can be determined from the relative intensities of the lines. For protons the shifts are of the order of a few parts per million, but for other nuclei the effect may be much greater; cobalt compounds, for example, show shifts of the order of 1 per cent. The relation between shifts and chemical environment provides a very powerful method of studying molecular structure, and this is being especially exploited in organic chemistry.

An investigation of diketene, for example, illustrates the possibilities of the method. The structure of this substance has been studied by a wide range of chemical and physical methods, and two formulations could explain the experimental observations:

$$\text{I} \quad \begin{array}{c} CH_3-C=CH \\ | \quad | \\ O-CO \end{array} \qquad \text{II} \quad \begin{array}{c} CH_2=C-CH_2 \\ | \quad | \\ O-CO \end{array}$$
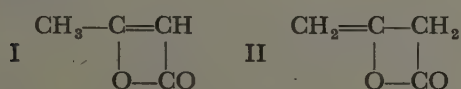
Structure I would give two proton resonance lines; one of intensity 3 from the CH_3 group, and one of

intensity 1 from the CH group. Structure II would give two lines of equal intensity from each of the two CH_2 groups. A drop of liquid diketene in fact showed two proton resonance lines of equal intensity in positions consistent with structure II, which is thus unambiguously identified [25]. Allinger [26] has recently measured the nuclear magnetic resonance spectrum of helvolic acid and some of its derivatives. Although this is a complicated organic compound having 32 carbon atoms, the spectrum provided crucial information which led to the final elucidation of the structure. Chemical shifts can be studied in many other nuclei and used for structural diagnosis and analysis. R. Freeman and R. E. Richards [27] have studied the gallium resonance in gallium dichloride. This substance is dimeric and diamagnetic, and could be formulated in two ways:

$$\text{I} \quad \begin{array}{c} Cl \\ \diagdown \\ Cl \diagup \end{array} Ga—Ga \begin{array}{c} \diagup Cl \\ \diagdown Cl \end{array} \qquad \text{II} \quad Ga^+[GaCl_4]^-$$
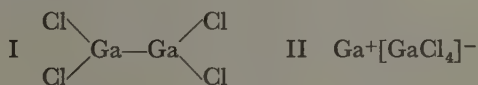
The liquid shows two gallium resonance lines, showing that it contains two different kinds of gallium atom and confirming Raman spectroscopic measurements which have been interpreted in terms of structure II [28].

MULTIPLET INTERACTION

Under higher resolving power the three main proton resonance lines of ethyl alcohol (from the methyl, methylene, and hydroxyl groups respectively) show fine structure (figure 5). This arises from a weak interaction and provides still further valuable information. The simplest molecule in which this so-called 'multiplet interaction' can occur is HD. The proton has a spin quantum number $I = \frac{1}{2}$, and for the deuteron $I = 1$; thus the proton can adopt two permitted orientations in the magnetic field and the deuteron three orientations. In the discussion of chemical shifts it was explained that a magnetic field can induce a weak uncoupling of valence electrons and produce a weak paramagnetism in them. The applied field, H_{appl}, induces this temperature-independent paramagnetism uniformly over the molecule, but the local field of the proton produces an additional effect in the bonding electrons, which modifies very slightly the field experienced by the deuteron. This additional effect depends on which of the two possible orientations the hydrogen nucleus adopts; the deuterons find themselves in one of two different fields, and consequently the deuteron resonance is a doublet. Similarly, the protons
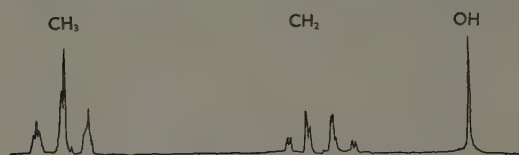
FIGURE 5 – *Proton resonance spectrum of ethyl alcohol at 30 Mc/s, showing fine structure arising from second-order interaction.*

experience a field that is modified by the additional paramagnetism induced in the bonding electrons by the deuteron. This induced field has three values, corresponding to the three orientations which the deuteron can adopt; consequently the proton resonance line is a triplet. The multiplicity of the resonance line of a nucleus or group of nuclei therefore reflects the number of orientations which the nuclei adjacent to it can assume. For example, in alcohol the methyl group is adjacent to the methylene group, which has two protons, each of which can have one of two orientations. The three different combinations of the methylene protons which the methyl group might 'see' are therefore

$$+\tfrac{1}{2}, +\tfrac{1}{2}; \quad +\tfrac{1}{2}, -\tfrac{1}{2}; \quad -\tfrac{1}{2}, -\tfrac{1}{2}$$
$$-\tfrac{1}{2}, +\tfrac{1}{2}$$
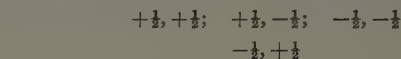
There are thus three lines, the middle one being twice as intense as the outer ones because there are two ways of arranging the methylene proton spins in this case. The methylene group experiences fields corresponding to the four possible ways of arranging the spins of the methyl group:

$$+\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{1}{2} \quad +\tfrac{1}{2}, +\tfrac{1}{2}, -\tfrac{1}{2} \quad +\tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{1}{2} \quad -\tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{1}{2}$$
$$+\tfrac{1}{2}, -\tfrac{1}{2}, +\tfrac{1}{2} \quad -\tfrac{1}{2}, +\tfrac{1}{2}, -\tfrac{1}{2}$$
$$-\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{1}{2} \quad -\tfrac{1}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}$$
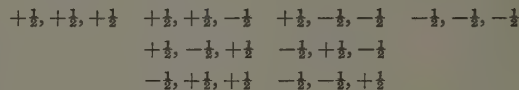
The intensities are this time in the ratio $1 : 3 : 3 : 1$. Thus not only can the presence of particular functional groups be identified in a molecule from the positions of the chemically shifted nuclear magnetic resonance lines, and their relative numbers measured from the relative intensities of the lines, but from the multiplet structures it is often possible to decide the relative positions of groups in the molecule. It is easy to see why this powerful tool has been received with such enthusiasm by many organic chemists.

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Electrolytes in plant tissue

R. N. ROBERTSON

The absorption of electrolytes by plant tissue has been the subject of much research not only because of its importance in the mineral nutrition of plants but also because its mechanism is not obviously explained by simple chemical concepts. The principal interest, from the latter point of view, is the capacity of plant cells to accumulate salts against a concentration gradient and their ability to discriminate between different, though similar, ions.

The simple picture of the plant cell shows a non-living, freely permeable cellulose wall surrounding the living part of the cell, the cytoplasm, which itself surrounds the non-living vacuole containing substances in solution with very little colloidal material. The cytoplasm is known to consist of a matrix or gel in which are embedded microscopically recognizable bodies. These bodies include a nucleus, plastids which in green cells contain chlorophyll, and mitochondria (figure 4). With the electron microscope smaller bodies termed microsomes are sometimes distinguishable, but these may possibly be derived from a rearrangement during fixation of an endoplasmic reticulum [11]. Somehow this cellular structure builds up an internal concentration of dissolved material, absorbs ions against the concentration gradient, and retains them in the cell. For example, a gram of carrot tissue will absorb almost all the salt from 17 ml of 0·005 M KCl in about 48 hours. During this time the concentration of KCl in the tissue rises to about 17 times the original external concentration and about 1000 times the final external concentration. Clearly, knowledge of the structure of the cell is essential to understanding how energy is expended for the absorption of the salt against a concentration gradient and how the absorbed salt is retained in the cell.

Early research on the absorption of non-electrolytes, particularly by E. Overton [20], suggested that substances which were more soluble in oils than in water were absorbed more readily than substances of similar molecular weight but relatively less soluble in oil. This led to the idea that living cells were surrounded by a membrane through which soluble substances would pass more readily if they were lipophilic or hydrophobic, an idea developed in great detail by R. Collander [5], J. F. Danielli [7], and others. Evidence based on the behaviour of a variety of cells suggested that the membranes consisted of orien-

tated lipoid molecules, and though probably only two or three molecules in thickness offered resistance to the passage of hydrophilic molecules and ions. The plant cell seemed no exception to the general rule that entry of non-electrolytes was controlled by some such membrane. Though the observations did not indicate which part of the cell was being penetrated by the dissolved substances, it was assumed, on inadequate evidence, that the membrane was at the surface of the cytoplasm adjacent to the cellulose wall. A membrane of similar structure, and hence offering high resistance to the movement of hydrophilic substances, might, however, occur at the interface between the cytoplasm and the vacuole. For the last ten or fifteen years many plant physiologists have believed in the existence of a highly resistant membrane at the outer surface of the cytoplasm and of another at the surface of the vacuole. Some workers, e.g. W. H. Arisz and G. E. Briggs, have never accepted the suggestion of a membrane of high resistance outside the cytoplasm, and recently evidence has been accumulating that there is no such membrane.

For some years plant physiologists at Cambridge have regarded the surface of the cytoplasm as having water-filled spaces continuous with the water-filled spaces of the cell wall and the intercellular space systems. In 1948 G. E. Briggs and R. N. Robertson [2] pointed out that the diffusion of salts and larger molecules through carrot tissue was restricted to the regions outside the vacuoles but not necessarily outside the cytoplasm. Indeed, the nature of the potential difference when salt is diffusing from one side of a carrot slice to another suggested that diffusion was taking place in tissue which contained a large number of non-mobile anions, such as would occur in either cytoplasm or wall. The portion of a cell or tissue into which the solute from an external solution can penetrate readily became known in Cambridge as the 'free space'.
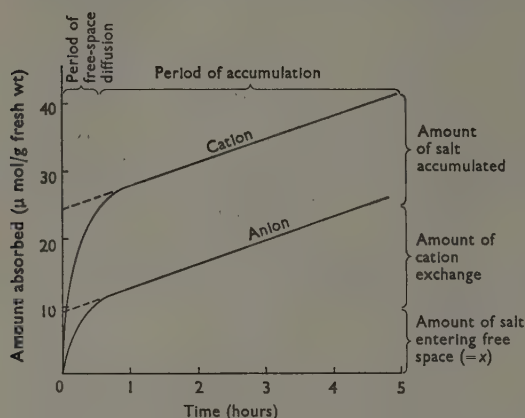
FIGURE 1 – *Diagram showing the variation with time of free-space diffusion, cation exchange, and accumulation.*

The concept of free space implies that the wall and cytoplasm of the cell allow free diffusion between the aqueous phases of the cytoplasm and the external solution (figure 1). The common observation that, when supplied externally, some intermediates of metabolism penetrate readily to the site of the reaction with which they are concerned is consistent with this view. Plant tissues will, for instance, respond readily to external application of acids of the Krebs cycle, indicating that these move rapidly into the cytoplasm. Since this space cannot be measured unless its properties relative to the method of measurement are defined, the concept of 'apparent free space' was introduced. Apparent free space was mentioned for the first time in publication by A. B. Hope and P. C. Stevens [14], with acknowledgment to Briggs, and in the last few years has been used by various investigators in the interpretation of their results [4, 15, 13, 9]. A discussion of apparent free space in relation to the physiology of the plant cell has been given by Briggs and Robertson [3] and a more detailed discussion by Briggs [1].

Apparent free space can be measured in various ways, but for present purposes it is sufficient to define it. If X is the estimated amount of solute (non-electrolyte or ion) taken up by the free space of cell or tissue from a solution of concentration C, then the apparent free space is X/C. In other words, the apparent free space is the volume by which the free space of the tissue appears to dilute the solution applied.

When electrolytes are used as the solute to measure the apparent free space, the free space behaves as though it contains non-mobile anions

balanced by mobile, mostly metallic, cations. From Donnan equilibrium considerations the non-mobile anions would be expected to exclude mobile anions, and so the entry of anions from the external solution would be restricted. On the other hand, since the cations of the external solution may exchange for the cations of the free space, the uptake of cations will frequently be greatly in excess of that of anions. If we were dealing with a simple Donnan system, the concentrations of the two ions would be given by the following equations:

$$[Cl^-]_i = \tfrac{1}{2}\sqrt{(a^2 + 4C_a{}^2)} - \tfrac{1}{2}a$$
$$[K^+]_i = \tfrac{1}{2}\sqrt{(a^2 + 4C_a{}^2)} + \tfrac{1}{2}a$$

where $[Cl^-]_i$ and $[K^+]_i$ are the internal concentrations of mobile anions and cations respectively, C_a is the external concentration of salt (assumed constant), and a is the concentration of non-mobile anions. The relationship of external to internal concentration would then be as shown in figure 2. In the plant cell, the free space contains a number of different non-mobile and mobile ions, but mobile cations, which can exchange with the cations of a salt applied externally, are always in excess of mobile anions. Such a difference between anion and cation absorption by the free space leads to the usual uptake relationship shown in figure 1. Thus if cation entry is used to estimate the apparent free space, high values are obtained compared with those based on anion uptake.
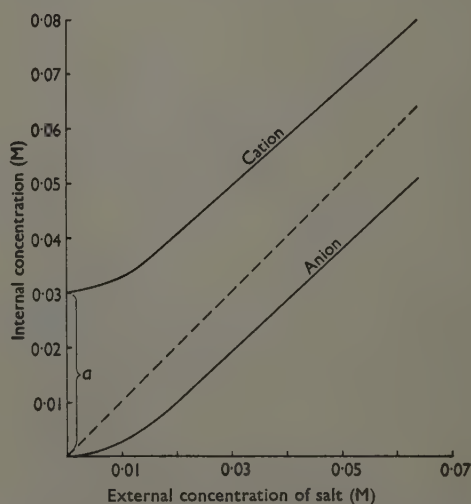
FIGURE 2 – *Graph showing the equilibrium concentration of mobile cations and anions in a phase containing non-mobile anions (a) plotted against the concentration of salt in the external solution.*

The surface of the plant cell consists of a cation-exchanging gel, similar to a cation-exchanging resin, which permeates both cell wall and cytoplasm, and realization of this allows various consequences to be discussed. The properties of the system depend on the concentration of the non-mobile anions (a), but estimation of this concentration is difficult. Early attempts to estimate the concentration from changes in the potential differences across cells or tissues with changes of salt concentration are too low by about an order of magnitude, through neglect of the divalent ions in cytoplasm and wall. A second method is to estimate the ratio of inside to outside concentrations of a particular ion: since divalent ions are more effective than monovalent ones in exchanging with ions already present, the ratios should be based on results with divalent cations. Calculations [3] from the data of W. Stiles and A. D. Skelding [24] suggest that the value of a may be as high as 0·4–0·6M.

There are many aspects of the concept of free space in cell wall and cytoplasm which cannot be discussed here, but the important idea is of the cytoplasm as a gel with structural rigidity due to the micelles of cytoplasmic protein. Non-mobile anions are part of this structural framework, which is rich in mobile cations and poor in mobile anions. While this system is adjusting itself to the addition of a salt, the process of accumulation begins.

'Accumulation', the term given to the results of 'active transport' against the concentration gradient, does not resemble the physical adjustment between cytoplasm and external solution just discussed. Though the process starts early in the physical adjustment between cell, cytoplasm, and external solution, accumulation continues for hours with very little change in rate, even though the internal concentration is increasing compared with the external. In dilute solutions the rate of accumulation increases with increasing external concentration, but it becomes independent of concentration in more concentrated solutions (figure 3). The rate of accumulation increases with temperature, the temperature coefficient suggesting that it depends on a chemical process. Since this process is dependent on expenditure of energy by the cell, any proposed mechanism must be related to respiration by which the cell derives its energy. Attempts to relate the process to respiration have led to a better understanding of what is involved but not, up to the present, to a proven explanation.

It was early shown that the respiration of certain tissues which had been washed for some time in water could be increased by the addition of salt; in carrot tissue, for instance, the rate of oxygen uptake increases by 70 to 100 per cent after the addition of 0·01M KCl. This increased respiration was originally called anion respiration by H. Lundegårdh and H. Burström [19], but the term 'salt respiration' is probably more appropriate. Conditions which vary the rate of this salt respiration proportionately vary the rate of accumulation. Inhibitors, such as cyanide, which stop the salt respiration without at the same time inhibiting the basal or ground respiration in water, completely inhibit the accumulation. The fact that this salt respiration is inhibited by carbon monoxide in the dark, but not by carbon monoxide in the light, shows that it is catalysed by cytochrome oxidase. The energy for the process appears therefore to depend on that part of the respiration system which is normally controlled by cytochrome oxidase.

While energy is necessary for continued accumulation against the concentration gradient, the same mechanism does not seem to be necessary to maintain the concentration once it has been built up. Thus, when the cytochrome oxidase is inhibited by carbon monoxide or cyanide, the salt which has been accumulated does not leak out to the exterior. This implies that the salt which has been accumulated has been transported to some region of the cell from which it cannot escape quickly. In plants like *Nitella*, which have unusually large cells, it is possible to remove the sap from the vacuole with a minimum of contamination by the cytoplasm. Analyses of this sap show
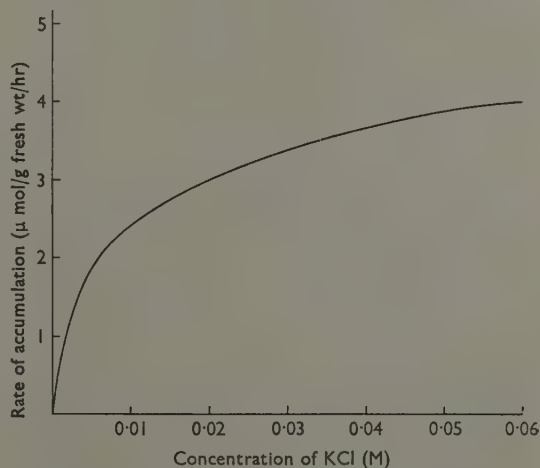
FIGURE 3 – *Graph showing the relation between rate of accumulation by sliced carrot tissue and concentration in the external solution* [23].

that accumulation has resulted in the salt concentration being increased within the vacuole: this suggests that energy is necessary to transport salt across the cytoplasm and through the membrane of high resistance which surrounds the vacuole. In ordinary plant tissue the cells are too small to permit easy analysis of the vacuole, as distinct from the cytoplasm, but indirect evidence from measurement of the impedance of these cells and of the increase in osmotic pressure following accumulation suggests that they too accumulate salt in the vacuoles.

Some years ago, Lundegårdh [17], impressed with the fact that the accumulation mechanism was dependent on a cytochrome type of respiration and that cations could exchange readily in plant cells, suggested that the mechanism might be an anion-carrier system depending directly on the cytochrome. His suggestion, in its simplest form, was that the cytochrome system, which carries electrons from the substrates of the respiration system to molecular oxygen at the surface of the cell, might function as a carrier of anions towards the centre of the cell, i.e. that unit negative charge in the form of an anion is carried in the opposite direction to unit negative charge in the form of an electron. If this were the mechanism, the maximum rate of accumulation would occur when one anion is transported into the cell for each electron transported to molecular oxygen. Lundegårdh thought that the hydrogen ions liberated from the substrate simultaneously with the electron passing to the cytochrome system would exchange for the cations in the external solution. In 1948 R. N. Robertson and M. J. Wilkins [22] showed that the rate of accumulation of salts approximated to, and did not exceed, the calculated rate at which electrons move through the cytochrome system.

Since Lundegårdh made his original suggestion we have acquired a much better understanding of the intracellular location of the enzymes which would be involved in such a mechanism. Lundegårdh originally thought that a membrane of orientated lipoid molecules probably occurred on the outside of the cytoplasm and that the mechanism of accumulation was located in this membrane. Since then, however, he agrees [18] that the evidence from the concept of apparent free space implies that the cytoplasm is in continuous aqueous contact with the external medium. Further, we now know that the cytochrome system in plant, as in animal, cells is associated with the mitochondria, bodies of about 1 µ diameter occur-

ring in the cytoplasm. If, therefore, the accumulation mechanism is closely associated with the cytochrome system, whether by the mechanism suggested by Lundegårdh or by some other, the activity should be demonstrable in the mitochondria, the reactions and physical properties of which can be studied after removal from the cell.

Since mitochondria are so near the limit of resolution of the light microscope, the examination of their internal structure has been possible only since section-cutting techniques became available for the electron microscope. In a study of the structure of plant mitochondria [10] it has been shown that mitochondria fixed in intact beet tissue and there sectioned show a double membrane round the outside, approximately 170 Å in thickness (figure 5). Internally not very much structure is apparent; some projections of the internal wall are similar to the cristae in animal mitochondria described by G. E. Palade [21] and others.

When the mitochondria are extracted from the tissue and then fixed, embedded, and sectioned ready for the electron microscope, some of the structure is lost, perhaps due to some swelling during extraction, but the membrane remains. R. N. Robertson, M. J. Wilkins, A. B. Hope, and L. Nestel [23] and S. I. Honda and R. N. Robertson [12] analysed extracted mitochondria, and showed that they constitute a Donnan system in which the mobile ions sodium, potassium, and (unless the mitochondria are extracted in the presence of a chelating agent) calcium, balance some non-mobile anions in the particle. If the mobile anion in the external solution is chloride, its concentration in the mitochondria is higher than would be expected on a Donnan adjustment, and often higher than in the external solution; this suggests that the mitochondria can accumulate.

The changes in internal concentration with time after a change in external concentration can be used to determine the diffusion constant of the salt in the membrane by applying Fick's law. From the half-times of adjustment, the diffusion constant of KCl in the mitochondrial membrane is calculated to be 1×10^{-13} cm²/sec. This means that the membrane on the outer surface of the extracted mitochondrion is about 10^8 times more resistant to the diffusion of KCl than is the same thickness of water. While it is at present impossible to say definitely that most of the resistance to diffusion in the mitochondrion is located in the
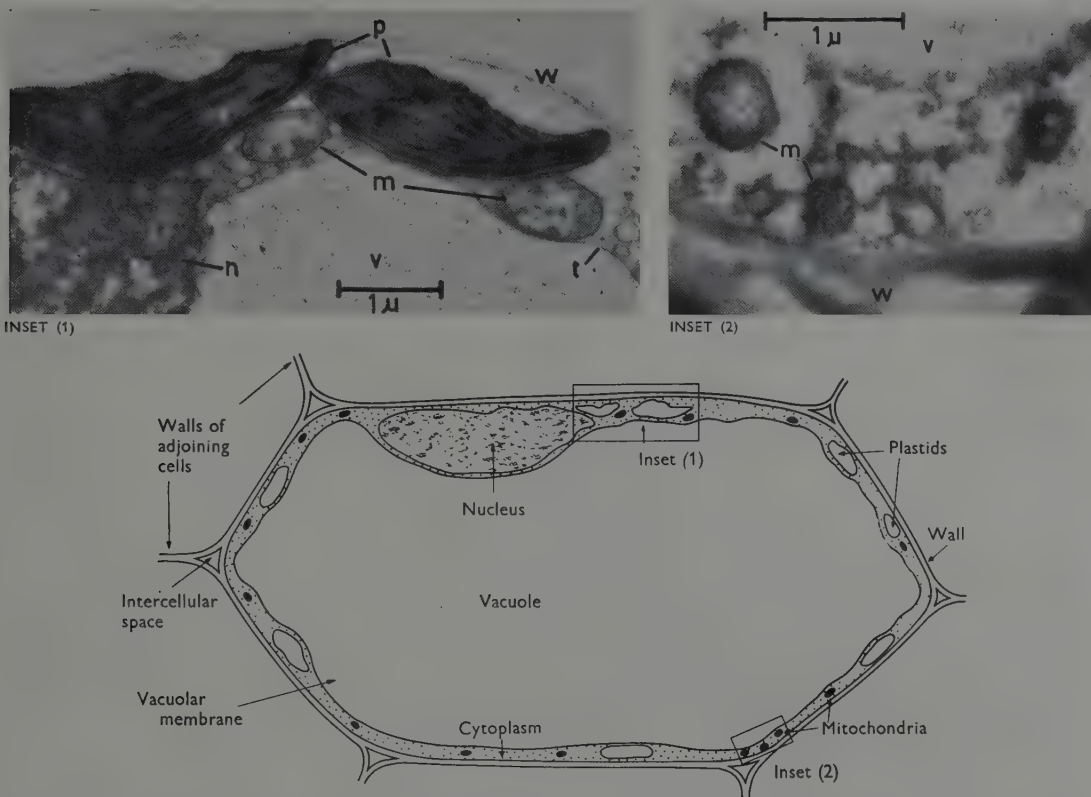
INSET (1)

INSET (2)

FIGURE 4 – *A diagrammatic representation of the plant cell. The inset electron micrographs show (1) portion of the nucleus, plastids, mitochondria, and membrane against the vacuole (unpublished micrograph of a young wheat-leaf cell by A. J. Hodge, F. V. Mercer, and J. D. McLean), and (2) mitochondria and wall (unpublished micrograph of a beet cell by J. F. Farrant, C. Potter, R. N. Robertson, and M. J. Wilkins). Key: n = nucleus, v = vacuole, m = mitochondria, w = wall, p = plastid, t = membrane.*

surface membrane, this seems a plausible supposition. If the resistance to diffusion were distributed evenly through the bulk of the particle, the average diffusivity would be 2×10^{-11} cm^2/sec. The mitochondrion therefore has the requisite property of a high resistance, which would act as a barrier to leakage of any salt which had been accumulated within.

It has already been mentioned that the mitochondrion seems to be capable of maintaining chloride internally in a higher concentration than would be expected from the Donnan relationship. Robertson, Wilkins, Hope, and Nestel showed that the concentration of chloride in the mitochondria was proportional to the oxygen uptake. Further, they calculated the rate of ion accumulation necessary to maintain the concentration of chloride internally, assuming leakage at the rate expected from knowledge of the diffusion constant.

They showed that the rate of accumulation would be of the right order of magnitude to correspond to the hypothesis of the relation to hydrogen and electron transport. In this connection it may be significant that many believe that the cytochrome system is located in the surface membrane of the mitochondrion. Perhaps it is here that the first stage of accumulation from the free space takes place.

The problem of accumulation by cells may therefore have become the problem of accumulation by mitochondria, but even if mitochondrial accumulation is found in subsequent work to be a general phenomenon, this does not necessarily mean that accumulation in the cell takes place in this way. Among the outstanding difficulties, for instance, is the transference to the vacuoles of salts accumulated by mitochondria. Very little is known about the relationship of mitochondria to the inner surface of the cytoplasm which borders
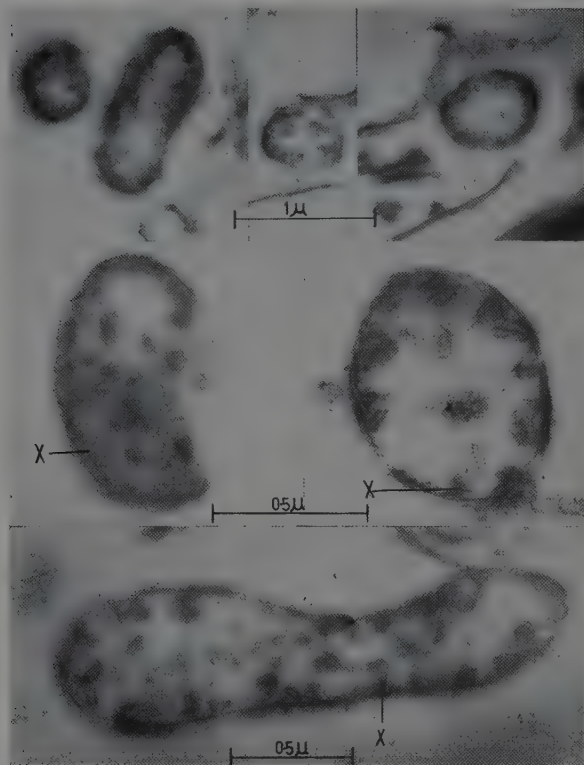
FIGURE 5 – *The morphology of mitochondria illustrated by electron micrographs of sections of red beet tissue* [10]. *Internal double membranes resembling Palade's cristae are to be seen at points marked X.*

on the vacuole, though mitochondria are seen to move readily in the protoplasm streaming round the cell and many of them frequently come into contact with the surface of the vacuole. It is possible that mitochondria would pick up ions in one part of the cell and, due to change in their metabolic activity, lose them in another.

From the point of view of comparative physiology, the secretion of HCl by the gastric mucosa of animals is of the greatest interest in relation to ion accumulation by plants. When hydrogen ions are passed to the lumen of the stomach, hydroxyl ions in equivalent amount form bicarbonate ions which pass to the blood. The evidence suggests that the hydrogen ions are those of respiration, and that the primary step is the separation of hydrogen ions and electrons at the cytochrome system (R. E. Davies [8], E. J. Conway [6]). Such separation occurring at an oxidation-reduction step, when an electron passes through a resonance system in a membrane impermeable to cations, may be the primary step in certain kinds of secretion. This hypothesis, however, does not necessarily fit all kinds of secretion; active transport of sodium through frog's skin, for example, definitely exceeds the rate calculated from the oxygen uptake (K. Zerahn [25], and A. Leaf and A. Rensham [16]). Perhaps eventually several mechanisms of active ion transport will be found.

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Decorative etching and the science of metals

CYRIL STANLEY SMITH

The revealing of structure by etching is a comparatively recent development in metallurgy. As this article shows, however, this possibility has for centuries been utilized by craftsmen making weapons such as swords and, later, gunbarrels. In this art the metalworkers of Europe were far behind those of the Orient. The products of Damascus were extensively distributed and widely famed, but the art found its highest expression in the seclusion of Japan.

The modern science of metallography was born on 28th July 1863, when Henry Clifton Sorby wrote in his diary, even though mistakenly, 'Discover the *Widmanstättischm* figure in [Lowmoor] iron'. It reached maturity four decades later, when Roozeboom applied the phase rule of Willard Gibbs to the many empirical observations that had accumulated in the intervening period. However, a long period of gestation had preceded birth, involving both philosophical speculations on structure generally and the use by scientists and craftsmen of fracture or etching to reveal something related to internal structure.

Figure 1 shows one of Sorby's photomicrographs which was shown at a British Association meeting in 1864, though not published until 1887 [1]. His first published illustrations were those impressed directly from deeply etched steel blocks in the columns of a Sheffield newspaper, probably in 1865[1] (figure 2). This technique, like its name, 'nature-printing', he had borrowed from the Viennese master printer Alois Auer, who in 1853 had published a demonstration of many kinds of typographic reproductions of things ranging from bats' wings and lace to etched stones and meteorites. A decade earlier P. M. Partsch's book on meteorites [2] had been illustrated with a print from an etched meteorite (figure 3) displaying beautifully the structure named after Widmanstätten, who had first revealed it by etching about 1807.

Etching had been used previously for other scientific purposes. In a paper which he claimed to have written in 1761, but which was not published until 1775, Grignon remarks that the intrinsic heterogeneity of iron can be shown by the action of acids [5]. J. J. Perret independently discovered this in 1771 [6], and following him the 'acid test' became a common means of distinguishing between iron and steel. In 1798 B. F. J. Hermann (see later) published illustrations of etched metal surfaces. In 1817 J. F. Daniell wrote 'On the Mechanical Structure of Iron Developed by Solution . . .' and clearly stated the importance of the subject and the value of macro-etching [4]. D. Kirkaldy, in 1862, published drawings (figure 4) of a number of etched samples of wrought iron and related the fibre structure to mechanical properties [3].

Behind this relatively modern work by scientists and engineers there was, however, a long history of etching by artisans to produce decorative surfaces.

THE PATTERN-WELDED BLADE

The damask or 'water' of Islamic swords is the best-known etched structural pattern. Most of our story will deal with Oriental metalwork, but it begins with a European technique of much interest, that of the Merovingian pattern-welded blade. These blades have been found in many Viking sites, but they were also used by Roman soldiers at the end of the second century and they are found widely throughout Europe in sites dating to the tenth century, when they suddenly cease. It seems possible that they all derive from a single source on the Rhine. Their manufacture and history have been reported in detail by A. France-Lanord [7]. From our present standpoint their interest lies in the rather complex welded patterns down the centre of the blades. Cassiodorus (*c.* A.D. 575), secretary to Theodoric the Ostrogoth, thus wrote to a Vandal king thanking him for a gift of some fine swords: 'Their centres have beautiful grooves cut into them, which seem to be

[1] The newspaper clippings themselves are preserved in a volume of Sorby's papers at Sheffield University Library. They are undated, but Sorby's diary shows that he was working on the process in March 1865.

covered with little worm-like markings. Shadows of such variety play there that you would suppose the metal to be interwoven rather than just reflecting different colours.'

The point of one of these swords, excavated from a sixth-century site in Lorraine and recently repolished and etched, is shown in figure 7. The pattern results from welding together piled strips of two different kinds of metal (carbon-free, and with about 0·15 per cent carbon respectively), twisting them, and then welding the twisted rods together side by side to form the core of the sword. The cutting edge is a thin layer of the same low-carbon steel, sandwiched symmetrically in iron which covers almost its whole extent. The necessary forging undoubtedly produced a better metal than a less complicated procedure would have done, and the marks evidently came to be regarded as a kind of identifying trademark of a superior sword. To be visible on the surface the patterns must have been developed by some kind of simple metallographic procedure, most probably by etching with a vegetable acid such as fruit juice or sour beer, or with a corrosive mineral like vitriol.[1]

Swords somewhat of this kind were being manufactured in Tibet in the nineteenth century. The centre of the blades consisted of a welded flat array of parallel rods of alternately hard and soft material bent in hairpin form. Although in some specimens the texture was revealed by very deep scraping following the lines of softer material and so producing a strong intaglio pattern, in others the texture was revealed only as a varying roughness resulting from transverse abrasion (figure 8).

THE ETCHING OF ARMOUR

In Europe, as has been noted, the production of these swords ceased in the tenth century, and others with higher carbon content and invisible texture took their place. Etching reappeared towards the end of the fifteenth century, when it was widely used for the etched decoration of armour, and, as an outgrowth of this, for the preparation of plates for intaglio printing [8]. Figure 6 shows a detail of a suit of armour made for the Duke of Brunswick about 1540. The design is entirely due to the artist's application or removal of an appropriate 'stop-off' to localize the chemical action, and the structure of the metal plays no role whatever.

It is indeed surprising that the armourers did not resurrect the idea of using decorative forged textures, but an examination of scores of pieces of European arms and armour has disclosed only a single example in which the texture of the metal is visible. This is a sword, made in Munich about 1540 (figure 5), that contains visible streaks due to forging an inhomogeneous metal. These streaks were probably unintentional, although they do in fact add substantially to the general pictorial effect in the etched area representing the sky.

It is surprising, too, that the coarse grain structure of cast brass, which is easily revealed by mild corrosion, has not been intentionally used decoratively. The spangle of galvanized iron is at least partially controlled with an eye to its appearance, and early in the nineteenth century a Frenchman named Alard made opera-glass cases, snuffboxes, and the like from an etched and lacquered tin plate which he called a *moiré métallique*. This was heat-treated to develop a large grain size, sometimes locally varied to give special patterns.

THE DAMASCUS SWORD

Compared with the relative neglect of structure by European metallurgists, the enjoyment and utilization of it in the Orient is impressive. There are two distinct lines to be followed. In one the patterns are produced by forging together metals of different composition; in the other, the more interesting, crystallization effects are used.

The famed 'Damascus' blades are of the latter kind [9]. The best were made in Persia from Indian steel. They were in use even before the Islamic period, for the kingly poet Imru'ul-Qais (died c. A.D. 540) refers to a blade having wavy marks like the tracks of ants. A younger contemporary of his, Aus ibn Hajar, describes blades in these terms: 'It has a water whose wavy streaks are glistening.' 'It is like a pond over whose surface the wind is gliding.' 'The smith has worked out in it a grain as if it were the track of small black ants that had trekked over it while it was still soft.'[2] For centuries thereafter the swords spread widely with the Islamic faith, and references to the ant tracks became a cliché among poets.

The making of these blades provided a great challenge to European metallurgical skill, for they are of very high carbon content (1·5–2·0 per cent) and difficult to forge. It was in fact not until 1823 that they were duplicated, by the French metallurgist Bréant. In 1840 Paul Annosov established

[1] J. W. Anstee, at the British Association meeting in Sheffield, 1956, reported the duplication of a blade of this kind using wrought iron alone, and remarked that the pattern could be seen on a polished blade without etching, supposedly as a result of local differences of slag content.

[2] The writer is indebted to Professor G. E. von Grünebaum for these early references and their translation.

a Russian factory for making them by Bréant's methods. Although Annosov understood their nature less clearly than Bréant did, he nevertheless makes a classic comment on the value of a visible structure in controlling production operations: 'Europeans have not had the experience of the Orientals in recognizing the modification which steel undergoes during forging. Their inferiority comes from the fact that they have no visible signs of these modifications before their eyes. But when they have to treat Damascus steel, they will soon come to understand the disadvantage of their in-experience, and each of them will know that the disappearance of the *moiré* at the forge represents an alteration of the metal attributable to the lack of skill on the part of the smith.' It is interesting to note that by this time Indian smiths had abandoned the art of handling very high carbon material, though they had learned to operate at higher temperatures and were melting steel of a lower carbon content, which is much easier to forge.

Figures 9–11 show some typical patterns on Damascus blades. The structure was developed on the polished surface by the use of a solution of a mineral called *zag* (probably a natural ferric sulphate), although a sixteenth-century Italian writer refers to the use of fruit juices for reviving the pattern on a worn blade. The dark- and light-etching areas are composed, respectively, of approximately eutectoid steel and approximately eutectic cast iron; the latter appears whiter because of its high concentration of iron carbide. The pattern derives directly from the structure of the cake of steel from which the blade was formed, and an essential part of the smith's skill was to forge at a temperature low enough to avoid re-solution of the carbon, and in such a manner that the structure of the ingot was not distorted beyond recognition. Simple compression would magnify the structure, while if the sword were drawn out without increasing in width, the structure would elongate into invisible fibres and the metal would become as uninteresting as any modern rolled piece of steel. An intermediate practice was evidently followed. The microstructures of transverse sections indicate that the finished sword was one-third to one-tenth the thickness of the casting, and there is rarely evidence of welding.

Although many of the most beautiful blades have an appearance that obviously originates in a section through a slightly distorted dendritic structure (figure 9), others (for example, figure 10) display the carbide network in a distribution and connectivity that could not be derived from the normal structure of a casting. There is, however, no doubt whatever that the structure of the cake of steel from which the sword is forged is basically responsible for the texture of the blade. The cakes, at least in India, where the steel was called *wootz*,[1] were made by intensely heating in a crucible a mixture of wrought iron—in the form of sponge, granules, or plates—with wood, the latter serving as the carbonizing agent. It seems to the writer most probable that the process was sometimes, perhaps often, not carried to the point of complete fusion, but only to the state of a mush of unfused grains of gamma iron surrounded by molten cast iron. Occasionally, indeed, plates of wrought iron seem to have been merely carburized and 'brazed' together with white cast iron and subsequently forged out, the grain resulting from the finished surface being cut so as to expose underlying lamellae.

Some of the most prized blades have lateral markings known as Forty Steps or Mohammed's Ladder, such as are shown in figure 11. Tschernoff suggested that these result from radial dendritic segration in the cake of cast steel used for forging the blade, but a close inspection of the pattern lends no support to this idea. It seems virtually certain that it was produced by cutting transverse grooves on the surface prior to the last stage of forging, so as to change the angle of intersection of the exposed lamellae, and hence their direction and spacing. The transverse markings on the kris to be discussed below were analogously produced.

ORIENTAL FORGED TEXTURES

In addition to the crystallization damask of the high-carbon swords, a simpler texture produced by forging alone was popular in the Near East and India, especially for the manufacture of gun-barrels. It was repeatedly, though erroneously, suggested in Europe that the true Damascus swords resulted in this way, and factories for the manufacture of composite forged blades were established in France, Italy, and Russia. A German metallurgist, B. F. J. Hermann, studying the problem in St Petersburg, read a paper [10] before the Russian Academy of Sciences in 1798 in which he gave what seem to be the earliest published illustrations of an etched metal surface (figure 12).

Both the earliest and the best work of this kind was Oriental. The most striking is the kris of the Malayan archipelago. The weapon seems to have

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[1] *Wootz* was made in India, notably in Hyderabad, Madras, and Mysore, from about the beginning of the Christian era.

originated in the thirteenth century in Java, with welded patterns appearing not later than the fifteenth century. Strong contrast was produced in the design by the use of steels differing greatly in corrosion resistance (including, it is said, meteoric iron, and in more recent times even nickel and European stainless steels); by forging at a low temperature to minimize diffusion; and by employing etching reagents such as fruit acids containing arsenic. Five different kinds of patterns are shown in figure 14. They all involved layering of the metal in a predetermined manner, and subsequent contouring of the piece by forging and cutting so that the layers would be appropriately sectioned on the final surface.

The most attractive and serviceable products of the mixed-metal forging technique were gunbarrels. Figure 15 shows a seventeenth-century Indian flintlock gunbarrel which was deeply etched to show in relief the contorted mixture of steels of different composition; figure 13 shows an eighteenth-century Turkish carbine, more sophisticatedly worked, and etched only enough to display the pattern. The manufacture of these so-called Damascus gunbarrels was established in Europe in the eighteenth century and, like that of the swords, had an important effect on European metallurgy.

The establishment of a factory in Sweden was described in 1773 by Peter Wäsström, who remarked on the effects of acid on different kinds of steel. Wäsström's paper aroused the interest of the great metallurgist Sven Rinman, who in the following year presented an extensive memoir [11] on the etching of iron and steel. He showed that when treated with acid, cast iron or steel always left behind a black sediment like black-lead, but that this was not found if the iron had been treated to remove phlogiston. He clearly anticipated, in everything except experimental elegance, Bergmann's more famous observations on the role of carbon in steel and iron, and though virtually unknown the paper is one of the classics of metallurgy.

Thus the duplication of an Oriental gunbarrel in a Swedish factory led to a metallurgist's study which inspired a chemist's investigation; this in turn was the basis for the formulation in France of a clear statement of the role of carbon in steel; this statement was an important factor in the Chemical Revolution. This sequence of events provides a fine illustration of the international and interdisciplinary factors involved in the growth of science.

THE JAPANESE SWORD

Japanese metalworkers understood the structure and nature of metals better than any others, and for centuries they made visible the structures of both ferrous and non-ferrous metals for both technological and aesthetic purposes. There was, unfortunately, no interaction with European science.

The Japanese sword is the supreme example of metallurgical art. It is composed of many layers of steel (often 2^{20}), worked by a complicated folding-welding-and-forging operation that uses a flux designed to remove the gangue from the crude metal and to control the carbon content [12]. The swords were given a final hardening while partially coated with a thermally insulating material that permitted the edge of the blade to be quenched rapidly while the body cooled more slowly and hence was not martensitic in structure. By adjusting the distribution of layers of steel of different hardenability, and by varying the outlines of the insulating compound, extremely wide ranges of surface patterns were produced, many of great beauty.

From certainly as early as the fifteenth century —and probably as early as the twelfth, and perhaps even earlier—the surface of these blades was finished by a sophisticated polishing operation that reveals the structure in almost metallographic detail. The finishing is said to have been done mechanically with a fine-grained limestone alone, but the appearance suggests that some chemical action may have been involved. It is unlike any European polish, for the harder material is definitely more matt than the soft, except in the intermediate zone where the two constituents are intermingled. The visible grain, which shows well in the unhardened portion of the blade surface, arises from variations of slag inclusions and carbon content in the different layers of metal as they are exposed at the surface. Details of a sword after a light repolish and metallographer's etch is shown in figure 16.

The writer has discussed the metallography of some of these blades in a recent paper [13]. An interesting feature is the presence of spots, known as *niye*, visible to the naked eye in the part of the sword that had cooled slowly enough to allow most of the material to become pearlitic. Figure 17 shows such spots on a sword polished in Japan, and figure 18 a similar one prepared metallographically. The spots are seen to be of martensite, resulting from abnormally large grains of austenite scattered through the metal.

The highest skills also were used in making the
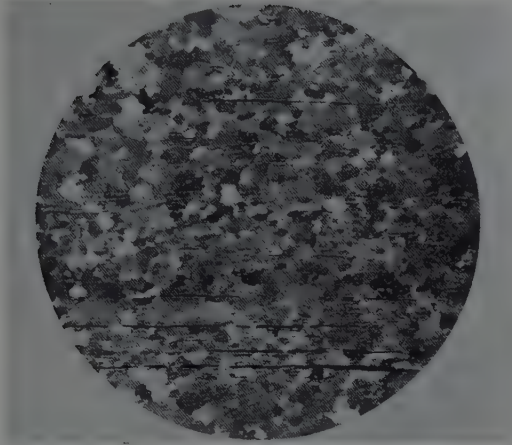
FIGURE 1 – *Photomicrograph of etched wrought iron, longitudinal section (Sorby, 1887). (× 9)*
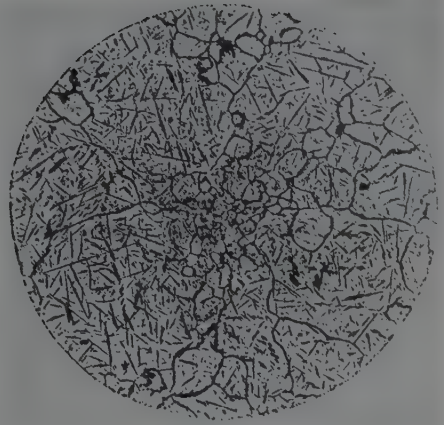
FIGURE 2 – *Direct nature-print from etched converted steel bar (Sorby, c. 1865). (Enlarged to 3/2 in reproduction.)*
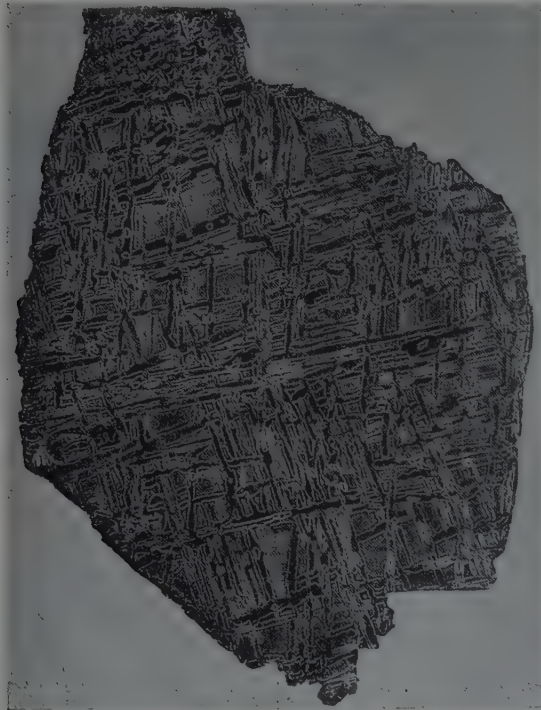
FIGURE 3 – *Typographical imprint of an etched meteorite (Partsch, 1843).*

BOWLING   DUNDYVAN

ROLLED-IRON

FIGURE 4 – *Texture of wrought iron developed by etching (Kirkaldy, 1862).*

FIGURE 5 – *Etched hunting sword made by Ambrosius Gemlich (Munich, 1540). (Natural size)*

FIGURE 6 – *Detail of etched breastplate of armour of the Duke of Brunswick*, c. 1540. (*Natural size*)
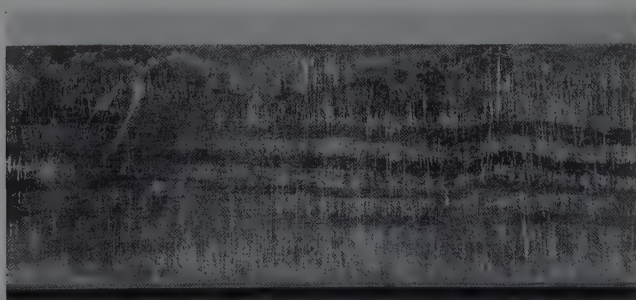
FIGURE 8 – *Sword from Derge, Tibet, nineteenth century or earlier (Chicago Natural History Museum)*. (*Natural size*)

FIGURE 9 – *Persian straight sword (Ispahan, eighteenth century). Damask shows distorted dendritic structure.* (*Natural size*)

FIGURE 7 (*Left*) – *Tip of pattern-welded blade (Lorraine, c. sixth century). Repolished and etched.* (× 1·14)
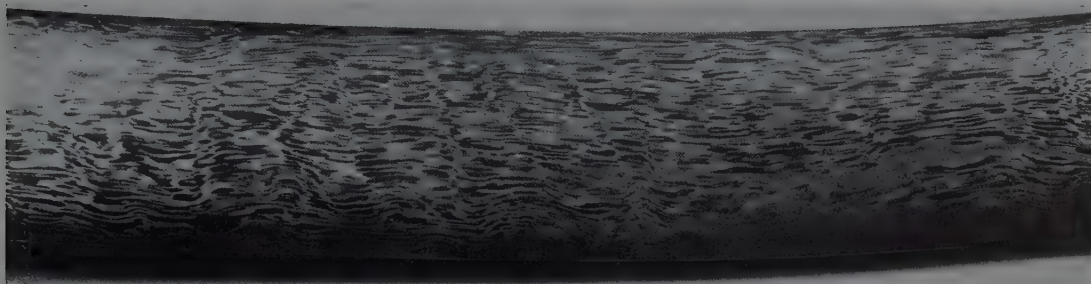
FIGURE 10 – *Persian sword, late seventeenth century.* (*Natural size*)

FIGURE 11 – *Persian sword of Indian form, with crossmarkings known as 'Mohammed's Ladder'.* (*British Museum. Photograph by courtesy of Mr Herbert Maryon.*)
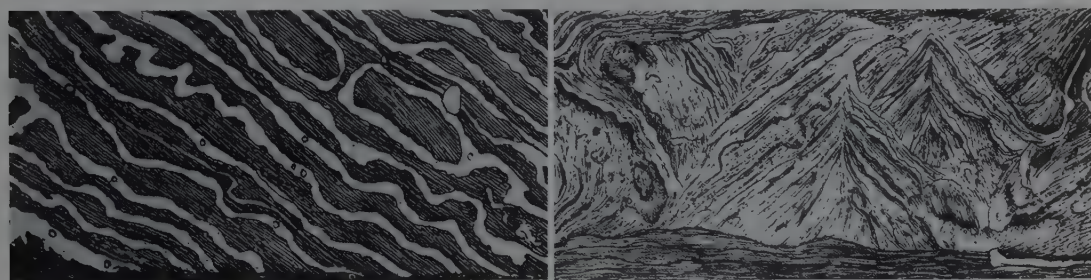
FIGURE 12 – *Artificial damask made by forging (Hermann, 1798). These are believed to be the first published illustrations of an etched metal surface.*

FIGURE 13 – *Barrel of a Turkish carbine, eighteenth century.* (*Victoria and Albert Museum.*) (× 1·1)

FIGURE 14 – *Blades of five Malayan kris.* (*British Museum.* *Photograph by courtesy of Mr Herbert Maryon.*)
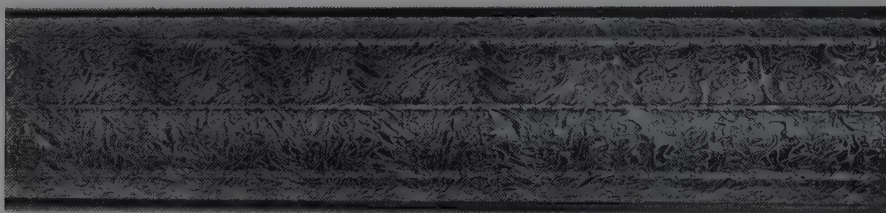
FIGURE 15 – *Barrel of flintlock gun* (*Indian,* c. 1650). (*Natural size*)
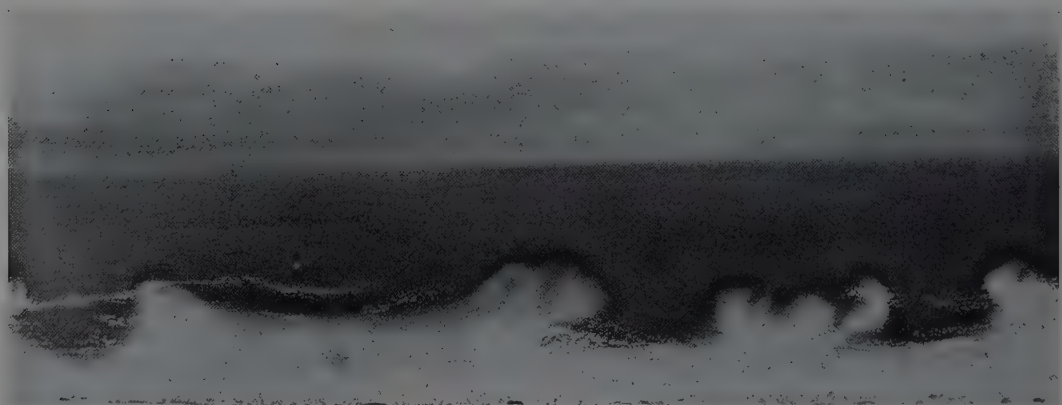
FIGURE 16 – *Unsigned eighteenth-century Japanese sword. Repolished and lightly etched.* (*Reproduced by courtesy of the* Associazione Italiana di Metallurgia.) (× 2·5)

FIGURE 17 – Niye *spots in sword by Masamune (1264–1343) with normal Japanese finish. (Collection of Capt. A. D. E. Craig.)* (× 85)
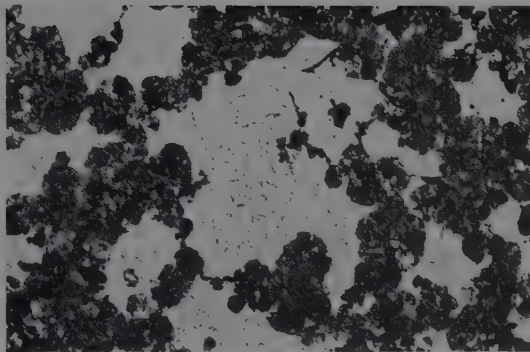
FIGURE 18 – Niye *spots on a sword by Nobuyuki (nineteenth century), metallographically repolished and etched.* (× 100)
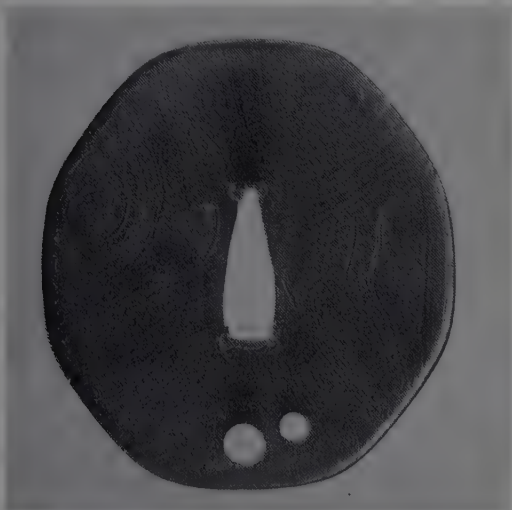
FIGURE 19 – *Iron* mokumé *swordguard, signed Miochin Munetane* (c. 1840).

FIGURE 20 – *Carved iron swordguard with* mokumé *texture, signed Tsugihide,* c. 1800. *(Victoria and Albert Museum.)*
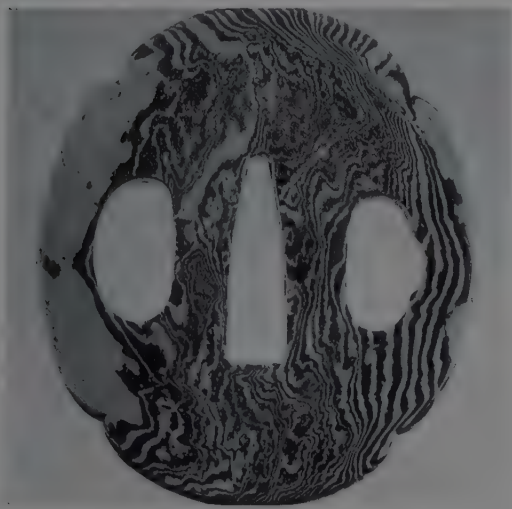
FIGURE 21 – *Soft metal* mokumé *swordguard. (Victoria and Albert Museum. Crown copyright.)*
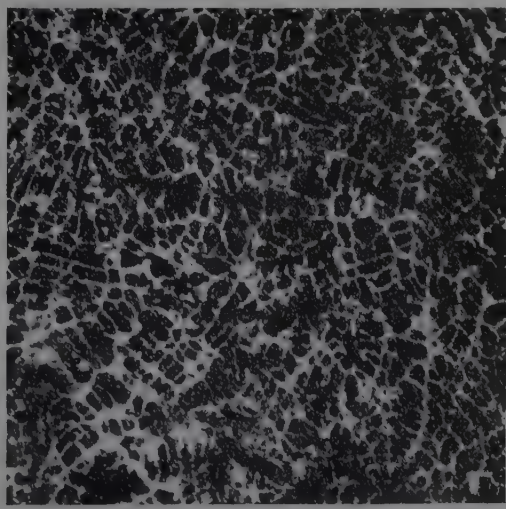
FIGURE 22 – *Original surface of a* shibuichi *swordguard, signed Masayuki* (d. 1769). (× 85)

fittings for the sword, particularly the guard (*tsuba*) and the little metal pieces at the two ends of the handle (*fuchi-kashira*). *Tsuba* made from the fourteenth to the seventeenth centuries were usually of iron and show a remarkable feeling for its nature. The earlier workers prided themselves on showing the very 'bones' of the metal. Surfaces would be proudly displayed showing marks from anvil roughness or pitting resulting from scaling or corrosion, sometimes accentuated with a few exquisite inlaid details in gold or silver. One of the most interesting techniques is that known as *mokumé* (woodgrain), which is related to that of the welded Damascus barrels and swords discussed above, though the designs are simpler and more pleasing. A mid-nineteenth century example is shown in figure 19. Figure 20 shows an iron guard made by forging together flat lamellae to give texture in the carved curved surfaces of the chrysanthemum petals.

In the eighteenth century and later, non-ferrous metals became common for sword furniture, usually finished by intricate chiselling, punching, and inlay. Several different copper and silver alloys were developed solely for the finely coloured patina that they show after suitable pickling, and these were sometimes combined to make the *mokumé* effect. One of these appears in figure 21. The dark areas are sectioned lamellae of the alloy known as *shibuichi*, an alloy of copper, containing approximately one-third silver, which has a re-markable greyish-green sheen unmatched in any other material. When properly pickled the eutectic network of silver-rich material stands in slight relief, simultaneously giving both the optical effect characteristic of the alloy and protecting from wear the patina on the copper surface. The alloy *shakado* (copper with about 4 per cent gold) also often shows a faint microstructure due to coring. Figure 22 is a photomicrograph of the surface of a *shibuichi* guard signed by a *tsuba* maker, Masayuki, who died in 1769. This is the original surface, finished approximately two centuries ago, yet it is little inferior to one that would be prepared today by modern metallographic techniques. Had such surfaces been available to seventeenth-century European microscopists, metallography would have begun then. Power, Hooke, and Leeuwenhoek could see no significant detail in surfaces distorted by scratching, burnishing, or fracture. Unfortunately, the greater sensitivity of Oriental metalworkers to the nature and structure of metals was largely aesthetic and was not paralleled by scientific speculation. It was in Sorby, as we indicated at the outset, that philosophy and craftsmanship first united.

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Crocuses

E. F. WARBURG

The evolution and classification of the various Crocus species presents several points of general interest to botanists, but the genus is one that has a much wider appeal. It is widely cultivated as a garden flower—where its bright coloration and generally early flowering make it particularly attractive—and a considerable range of varieties has been developed. Some further development of cultivated forms seems possible, especially within the *chrysanthus* group, which has permitted the introduction of a series of blue flowers.

The genus *Crocus* consists of some 80 species with their main centre in the eastern Mediterranean region. Several species occur in Spain and north-west Africa, but the number of species in comparable areas increases eastwards, the largest number occurring in the Balkans and Asia Minor. The most easterly species, *C. alatavicus*, is an outlier in the Alatau mountains in central Asia. The most northerly species, *C. caeruleus* (*C. albiflorus*), occurs high in the Alps. None is native in Britain.

Saffron, obtained from the styles and stigmas of *Crocus sativus*, is the only product of economic importance derived from any species of the genus. This species is cultivated in the greater part of the Mediterranean area and eastwards to Kashmir. It has been cultivated from ancient times and was formerly used for its medicinal as well as for its flavouring and colouring properties, which are still so widely esteemed. The word *Crocus* is of ancient Semitic origin, the word taking the form κροκος in ancient Greece. The word 'saffron' is of Arabic origin. Both words were originally applied to both the plant and the drug, the differentiation existing today being comparatively modern.

The origin of the cultivated saffron is not known. No plants having both the large flowers and long stigmata of the cultivated plant are known in the wild state, but allied plants extend from Italy to Persia. No doubt the cultivated saffron, which is very uniform throughout its range, was derived from one of them. It is completely sterile, seed not being produced. It has been shown to be triploid ($2n = 24$) with very irregular meiosis, so that the sterility is accounted for. Allied diploid forms are known. In England the true saffron was formerly cultivated in the eastern counties, especially in the area round Saffron Walden in Essex, which takes its name from the plant.

It has been suggested by W. B. Crump and W. A. Sledge that another species, *C. nudiflorus*, was also grown for saffron, particularly in the Midlands,

and that it was introduced there by the Knights of St John. *C. nudiflorus* grows well and is one of the very few species that spreads by stolons and not only by splitting of the corm or by offsets. It has thus become naturalized in England in meadows in a number of places within the area of its former cultivation. Its native area of distribution is in the Pyrenees and Spain. It was first recorded as a naturalized British plant at Nottingham in 1738. Although this species has considerably smaller styles and stigmas than *C. sativus*, the latter does not, as a rule, flower freely in England and demands special conditions: a preference for *C. nudiflorus* would therefore be understandable.

Crocuses have long been cultivated in Britain as garden plants. In J. Gerarde's 'Herball' (1597) crocuses are described that are clearly *C. vernus*—a name conveniently used in an aggregate sense for a group of species and their garden descendants—and *C. flavus* (*C. aureus*). Another is possibly *C. versicolor*, and there are at least two autumn species, *C. sativus* and probably *C. nudiflorus*.

In J. Parkinson's *Paradisi in Sole* (1629) 27 spring-flowering and four autumn-flowering kinds are enumerated. Most of the spring-flowering ones are varieties of *C. vernus*, but there are also—besides *C. flavus*—*C. angustifolius* (*C. susianus*), *C. biflorus*, *C. versicolor*, and possibly *C.* × *stellaris*. The autumn ones are difficult to identify, but they include *C. sativus*, *C. nudiflorus*, and probably *C. serotinus*. Crocuses were also much cultivated in Holland and are described in a number of Dutch books of the seventeenth century; the same species seem to have been grown in both countries.

In J. Sabine's account (1830) of the spring Crocus then grown in the garden of the Horticultural Society—two hundred years after Parkinson—no fresh species occurs, although the number of garden forms grown had increased enormously (57 varieties of *C. vernus* are enumerated). This is rather remarkable, because, though the species

then already in cultivation—with the exception of the south Russian *C. angustifolius*—are reasonably accessible in nature, they are no more so than a number of other species that were ignored.

These early cultivated species are conveniently considered separately.

C. vernus. This name is conveniently applied collectively to a group of closely allied plants, variously regarded by different authors as species or subspecies. The form most closely resembling the cultivated plants is *C. purpureus*, which occurs in a wild state in central Italy. This species is probably responsible, at least mainly, for the Dutch white, purple, and striped Crocuses that are today (with the Dutch yellow) the members of the genus most commonly grown in gardens.

C. caeruleus, a much smaller plant from the Pyrenees, Alps, and other European mountains, may also have played a part, but it is not very easy to grow and is not commonly grown today. Despite its name, it is usually white-flowered in nature. *C. vernus* is of variable colour in the wild, and differently coloured forms were in cultivation at an early date. The numbers of varieties increased rapidly and were given vernacular names by the Dutch growers, at least as early as Sabine's time, though he himself unfortunately gave nearly all of them Latin ones. Development has continued more slowly of recent years, and it would probably now be more difficult to get together a collection of 57 named varieties than in Sabine's time. Like *C. nudiflorus*, *C. vernus* has long been naturalized in Britain, being first recorded from Nottingham in 1796. These naturalized colonies —for example, one still existing in south Berkshire that has been known since soon after 1800—give a picture of the earlier forms. Modern forms (figure 17) differ little except in their larger size.

No wild form of this group appears to have been examined cytologically, but studies on cultivated varieties, mainly by K. Karasawa, who is responsible for most of the cytological work on the genus, indicate that the diploid number is 16. This number is found in some garden forms; others show the triploid number 24 or the tetraploid number 32, and there are a smaller number of aneuploid forms with various numbers between 18 and 30. As with many other garden plants (*e.g. Narcissus*), an increase in chromosome number is correlated with an increase in size, and large-flowered varieties—e.g. 'Excelsior', whose diploid number is 29 —tend to have high numbers. These garden varieties are largely fertile and so give rise to fresh forms. No detailed study appears to have been made on the relation between number of chromosomes and fertility, but the high fertility is, no doubt, part of the reason for the large number of varieties.

Most of the striped varieties show an irregular type of striping, not known elsewhere in the genus. They also frequently have somewhat misshapen flowers, occurring unexpectedly among purple clones. The striping is possibly due to a virus similar to that causing 'breaking' in tulips, but the matter has not yet been properly investigated.

C. flavus. This species, better known as *C. aureus*, is a native of the Balkans and western Asia Minor and was probably introduced into cultivation by the Dutch botanist Clusius in 1579; it was certainly in cultivation in 1665. Today it is represented in gardens chiefly by 'Dutch Yellow', though wild forms (figure 8) and a much paler variety, *sulphureus*, are also grown. The wild plant appears to vary little except in the depth of colour. 'Dutch Yellow' is a relatively robust plant and is completely sterile. It is now represented by at least three clones, differing in the colour and markings of the flower. Besides *sulphureus*, a number of other varieties—such as the cream-white *lacteus*—were formerly grown. Sabine lists nine varieties in all, but these have now almost, if not quite, disappeared from cultivation. There seem to have been no fresh developments in *C. flavus* during the last hundred years.

The diploid number of *Crocus flavus* is 8. Two clones of 'Dutch Yellow' have been reported to have numbers 14 and 15 respectively, with very irregular meiosis. The sterility of this plant is thus accounted for. Its origin must have been complex, perhaps resulting from tetraploidy followed by chromosome loss: hybridity is scarcely likely to be responsible on historical and morphological grounds. Nothing appears to be known about the reason for the sterility of *sulphureus*, whose diploid number is 8, which is normal for the species.

C. angustifolius (*C. susianus*). Like *C. flavus*, this species, yellow with brown markings on the outside, appears also to have been introduced by Clusius, but at a rather later date (1587). Parkinson describes two forms, differing in the markings of the outer perianth segments, and uses the name 'Cloth of Gold', by which the species is still known. There are still two forms in gardens, grown under the names 'susianus' and 'susianus minor': these appear to be those known to Parkinson. 'Susianus minor' has a diploid number of 12, with normal meiosis; '*C. susianus*' has a diploid number of about 15, with irregular meiosis, so that it is probably a

garden derivative of the former. No further variation appears to have taken place.

C. × *stellaris*. This was known to A. H. Haworth (1809) and very probably also to Parkinson. It is not known wild. J. G. Baker, in 1873, seems to have been the first to suggest that it was a hybrid between *C. angustifolius* and *C. flavus*; it is morphologically intermediate between the two and completely sterile. It has a diploid number of 10, to be expected in a hybrid between the normal forms of these species. According to Karasawa, no chromosome pairing takes place, so that its suspected origin is strongly confirmed by its cytology.

C. versicolor. This species is a native of the French and Ligurian Riviera. It was early cultivated and was formerly represented in gardens by a number of forms—Sabine gives 18—but, perhaps because of the introduction of other rather similar species, these have almost entirely disappeared. It is now mainly grown in two forms, both white but with differently marked purple lines on the outside of the perianth segments. In nature, the species is prevailingly lilac-flowered, and the persistence of the white forms in cultivation is perhaps due to their greater difference from related species (e.g. *C. minimus*, figure 6). Both diploid ($2n = 26$) and triploid forms are known.

C. biflorus. This is a member of a taxonomically difficult group of Crocus distinguished by the coats of the corms having horizontal rings round them (annulate) and by their spring-flowering habit. A group of autumn-flowering species with similar corms, including *C. speciosus* (figure 10), may not be closely related. Other members of the group will be considered later. *C. biflorus* itself is a native of Italy but is represented by a number of allied forms, variously regarded as varieties or distinct species, in the Balkans and Asia Minor. All the early cultivated forms, however, resemble the Italian plants and probably originated from them. They have white or pale lilac flowers, variously striped with dark purple on the backs of the outer segments. One of them (var. *parkinsonii*, figure 5), originally named by Sabine, is believed to be the same as a form known to Parkinson. Another old form, known as the 'Scotch Crocus', is quite sterile, like several other old garden Crocuses. Both these and several other varieties are still frequently grown. Three varieties in this group have a diploid number of 8. The 'Scotch Crocus', perhaps the most unlike the wild types, has apparently not been cytologically examined, and the reason for its sterility is not known.

A recent variety, 'Barrii', most like this group,

has a diploid number of 7 and some peculiar features in the corm tunic. Possibly it is a hybrid with one of the 6-chromosomed species of the Aureus group (e.g. *C. balansae* (figure 14), though this species is not itself a likely parent of 'Barrii').

Throughout this period, and indeed later, the autumn-flowered species, though at least three were grown, seem to have shown little variation. Whether these species are inherently less variable than some of the spring ones, or whether the lack of variation is merely a reflection of lack of interest is uncertain. The autumnal species seem never to have been as popular as the spring ones.

Since 1830 the number of species in cultivation has increased enormously, largely due to the efforts of three English horticulturists and amateur botanists, W. Herbert, G. Maw, and E. A. Bowles. Each of them collected together in their gardens as many different species of the genus as they could, and each produced a monograph on the genus (Herbert, 1847; Maw, 1886; Bowles, 1924 and 1952). Most of these species, though some of them are variable in nature, have not become the parents of new garden races, but there are developments from two of them worth considering further.

C. tomasinianus. This species was named by Herbert after its discoverer, Tommasini of Trieste, who sent bulbs to both Herbert and Maw. It grows wild in Jugoslavia. It is closely allied to *C. vernus*, differing from the latter mainly in its narrower leaves and narrower, more pointed, flowers. Of all species of Crocus it is the most at home in English gardens, sowing itself freely. Typically, the flower is lavender inside and grey outside; but it has varied considerably, and several selected forms are now sold; an example is 'Barr's Purple' (figure 15). It has a diploid number of 16.

During this century plants that appear to be hybrids between *C. tomasinianus* and *C. vernus* have appeared in gardens; they are usually named as if varieties of *C. vernus*. They combine the larger flowers of garden forms of the latter with the early-flowering habit and flower coloration of *C. tomasinianus*. Two in commercial cultivation are 'Vanguard' (figure 16) and 'Haarlem Gem'. 'Vanguard' is a triploid ($2n = 24$), which is consistent with its being a hybrid between *C. tomasinianus* and a tetraploid garden form of *C. vernus*.

C. chrysanthus (figures 3, 18–20). This species is an ally of *C. biflorus*, having a similar corm and, commonly at least, the same chromosome number ($2n = 8$). It differs in the colour of the flower, typically of the same golden yellow as is met with in other Crocuses (e.g. 'Dutch Yellow'), the shape
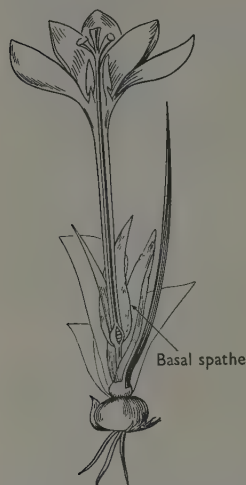
FIGURE 1 – *Diagram of crocus, showing basal spathe.*
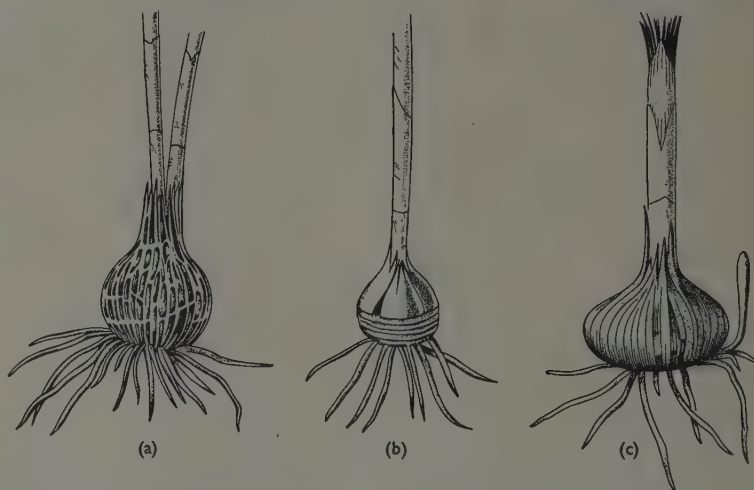
FIGURE 2 – *Crocus corms.* (a) *reticulate tunic;* (b) *annulate tunic;* (c) *tunic of parallel fibres.*

of the flower and the almost constant presence of a black barb at the bottom of the anthers. It is a native of the southern and western Balkans and of Asia Minor. It varies very much in nature in flower size and in colour; the latter varies from deep yellow to white, with or without external colouring. Many forms have been selected and given names; 'E. P. Bowles' (figure 3) is one.

The origin of such plants presents no difficulty, but that of other forms usually named as varieties of *C. chrysanthus* is less simple. Thus, var. *fuscotinctus* (figure 20), originally described by Baker (1873), differs not only in its differently shaped flowers with the anthers uniformly grey and without black barbs but also in its chromosome number ($2n = 10$). 'Canary Bird', which looks like a derivative of it, has the same number and a nearly regular meiosis. It seems reasonable to think that these forms represent another species; they do not, however, seem to be known in a wild state.

The situation in this group is further complicated by other species. These include *C. aerius*, with blue flowers; two plants variously regarded as separate species or as varieties of *C. biflorus*— *C. weldenii*, a Balkan plant with flowers pure white within and uniformly purplish (or white) outside; and *C. adami* from Asia Minor with blue flowers, striped outside.

Garden plants of the *weldenii* type—called '*weldenii*', '*weldenii albus*' (figure 4), and 'Kittiwake' respectively—were found by Karasawa to have diploid numbers of 15, 20, and 15. The first of these is thus scarcely likely to be the wild plant.

The numbers suggest, however, that a species distinct from *biflorus* is involved. It is highly desirable that wild *weldenii* material should be examined cytologically.

Many varieties of this annulate group have appeared and continue to appear. Though these are usually named as forms of *C. biflorus* (including *weldenii*) or *C. chrysanthus*, it is probable that many of them are, in fact, of hybrid origin. Of special interest are the so-called blue forms of *C. chrysanthus* (e.g. 'Blue Pearl', figure 18). These have introduced a new colour range into garden crocuses. The only wild form of this species to show bluish coloration is var. *caerulescens*, which may itself be a hybrid with *C. aerius*; it shows the bluish colour only on the outside of the flower. It seems very possible, therefore, that these blue forms, though resembling *C. chrysanthus* in flower shape and the black barb on the anthers, are hybrids with *C. aerius* or *C. adami*.

Developments in the garden Crocus in the near future are likely to be concerned mainly with this group, and if the size of their flowers is increased further they may well become as popular as the forms of *C. vernus* and 'Dutch Yellow'.

CLASSIFICATION

As reference has been made above to relationships between species, a little ought to be said, in conclusion, about the classification of the genus. It has proved difficult to devise any system without an arbitrary element. The most satisfactory system is that of Maw, who uses, in this order, the following

FIGURE 3 – C. chrysanthus '*E.P. Bowles*'.

FIGURE 4 – *The plant known in gardens as* 'C. weldenii albus'.

FIGURE 5 – C. etruscus '*Zwanenburg Variety*' (*blue*) and C. biflorus *var*. parkinsonii (*white*).

FIGURE 6 – C. minimus.

FIGURE 7 – C. sieberi *var*. atticus.

FIGURE 8 – C. flavus (C. aureus).

FIGURE 9 – Crocus medius.

FIGURE 10 – C. speciosus.

FIGURE 11 – C. asturicus *Atropurpureus*.

FIGURE 12 – C. longiflorus *var*. melitensis.

FIGURE 13 – C. byzantinus.

FIGURE 14 – C. balansae *'Zwanenburg Variety'*.

FIGURE 15 – C. tomasinianus *'Barr's Purple'*.

FIGURE 16 – C. tomasinianus × vernus *'Vanguard'*.

FIGURE 17 – C. vernus, *a modern purple form*.

FIGURE 18 – C. chrysanthus *'Blue Pearl'*.

FIGURE 19 – C. chrysanthus *'Zwanenburg Bronze'*.

FIGURE 20 – C. chrysanthus *var.* fuscotinctus.

qualities: (1) Presence or absence of a 'basal spathe' (figure 1)—a whitish bract from the top of the corm, subtending the inflorescence; (2) the type of corm coat (figure 2), whether of parallel fibres, reticulate, annulate, or interwoven into a sort of herring-bone pattern; (3) vernal or autumnal flowering; (4) flower colour. Even this system is not very satisfactory. Thus there is a group of probably allied species called by Bowles the 'Imperati Group' (including *C. minimus* (figure 6), *C. etruscus* (figure 5), and *C. versicolor*). They are recognizable by their flowers being lilac (or white) inside and usually buff outside with purple stripes; by a geographical range from the Balearic Isles through south France, Corsica, and Sardinia to Italy; and by chromosome numbers 22, 24, and 26 (numbers which also occur in species morphologically very unlike this group). Although the members of this group all have a basal spathe, *C. dalmaticus*, which lacks one, appears to be closely related to them; a further complication is that it includes some species with parallel corm-fibres and others with reticulate ones.

A more satisfactory group from the point of view of Maw's classification is the 'Aureus Group' of Bowles, e.g. *C. balansae* (figure 14) and *C. flavus* (figure 8). These are all characterized by a parallel-fibred tunic, no basal spathe, and yellow flowers (except in some forms of *C. candidus*) produced in spring. They have an eastern Mediterranean distribution and usually a diploid number of 6 (5 species), rarely 8 (*C. flavus*). *C. korolkowii*, however, is exceptional in both distribution (Turkestan) and chromosome number ($2n = 20$); though sharing the other features of the group mentioned it may not be closely related.

No sharp line can be drawn between autumn and spring species. Flowering of different species ranges from September to April or May, and the autumnal species vary much in the time of production of their leaves. Some species, e.g. *C. speciosus* (figure 10) and *C. byzantinus* (figure 13), flower in the autumn and produce their leaves in spring; others, e.g. *C. medius* (figure 9), produce their leaves at the end of the flowering period. Others again, e.g. *C. asturicus* (figure 11), have the leaves

above ground but short. Finally, some species e.g. *C. longiflorus* (figure 12), have them fully developed.

Blue and yellow flowers are never found in the same species (with the possible exception of *C. chrysanthus*). White forms of blue-flowering species are frequent, of yellow-flowering species rare; some species are always white. Flower colour is sometimes more or less constant in a group of related species (e.g. the 'Aureus' or 'Imperati' group), but in such groups as the *Biflorus-chrysanthus* group, already discussed, it is very variable.

The general impression given by the genus is firstly of a few isolated species without close allies. Perhaps the most striking of these is *C. byzantinus* (figure 13). In this the members of the two perianth whorls are very different in size, the inner being much smaller and erect, so that the flower recalls an Iris. On this account it has been put in a separate genus *Crociris*, but hardly justifiably. Other unusual features of this plant are its purple style and stigmas, and its preference for shade.

Secondly, there are some well-defined groups, like the *biflorus–chrysanthus* alliance with annulate corm tunics and a group of two autumn species having similar corms (*C. speciosus* (figure 10) is one of the latter).

There remains a large number of species without any very striking characters. Many of these fall into rather ill-defined groups like the 'Imperati' group, which is connected by *C. dalmaticus* to such species as *C. sieberi* (figure 7); this has flowers similarly coloured on both sides, a yellow throat, and a strongly netted corm. Some species like *C. medius* (figure 9), though without any particularly unusual features, have no obvious relatives.

Chromosome studies have not so far helped very much in classification. Certain groups, such as the 'Aureus' group, are distinctive, but many species —some of them very distinct morphologically like *C. byzantinus*—have diploid numbers in the 20–26 range. No genetical work has been done on *Crocus*, and hybridization experiments might throw further light on the interrelationships. However, it seems impossible with the present information to get any picture of the probable evolution within the group nor to devise a really satisfactory classification.

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New techniques for the study of enzyme mechanisms

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The importance of enzymes in regulating the complex system of chemical reactions which characterizes living cells needs no emphasis. Although the overall course of many enzyme-catalysed reactions is now well known, many details of the reaction mechanisms have still to be elucidated, and to do this new techniques have had to be evolved. These are of two principal types: methods for the identification of transient intermediates, and study of the kinetics of the reaction during the time, often extremely short, before a steady state is established.

INTRODUCTION

Enzymes are catalysts with a dual function in biochemical processes: by virtue of their specificity they select one of several possible reaction paths and they accelerate the rate of the chosen one without affecting the final equilibrium. All enzymes purified and characterized so far have been shown to be proteins. Some enzymes have a prosthetic group or coenzyme—such as haem or riboflavin derivatives—associated with the protein moiety, while others contain nothing but the amino acids of the protein structure. An understanding of the mechanisms of enzyme actions is essential to an understanding of how the complex biochemical processes of living cells are co-ordinated, and in recent years a number of important new techniques have been developed for the study of enzyme mechanisms.

One of the earliest and most fundamental concepts for the interpretation of enzyme-catalysed reactions was that developed by L. Michaelis and M. Menten [1]. They found that on increasing the concentration $[S]$ of the substrate—the substance on which an enzyme acts—the rate of an enzyme-catalysed reaction increases up to a constant maximum velocity V_{max}, depending on the enzyme concentration $[E]$ and a constant k which depends on both the nature of the enzyme-substrate system and the physical conditions of the experiment. This relationship shows that compounds of enzyme and substrate (ES) are formed and that these then decompose into enzyme—thus made available for further reaction—and products (P):

$$\text{Enzyme} + \text{substrate} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Enzyme/substrate}$$

$$\overset{k}{\rightarrow} \text{Enzyme} + \text{products} \quad \dots (1)$$
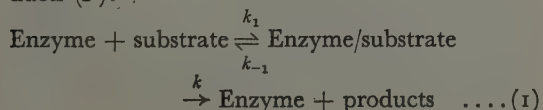
By the Law of Mass Action the Michaelis constant K_m can be expressed as:

$$K_m = \frac{[E][S]}{[ES]} = \frac{k_{-1} + k}{k_1} \quad \dots (2)$$

From (1) and (2) it can be shown that the velocity V of the reaction can be expressed as:

$$V = \frac{d[P]}{dt} = \frac{k\,[E]_0\,[S]}{K_m + [S]}$$

where $[E]_0$ is the total concentration of enzyme, i.e. both free and combined with substrate. When $[S]$ is very large compared with K_m, all the enzyme is in the combined form, and

$$V = V_{max} = k\,[E]_0$$

Under any given set of conditions K_m and V_{max} (and also k if the molar concentration of enzyme is known) are normally easily determined by plotting $1/V$ against $1/[S]$ and evaluating V_{max} at $[S] = \infty$ from extrapolation to $1/[S] = 0$.

The Michaelis constant can often be used as a measure of the specificity or affinity of an enzyme for various substrates. From equation (2) it can be seen that the relative magnitudes of k and k_1 decides whether K_m is a true equilibrium constant, and therefore a measure of the binding energy of substrate and enzyme, or whether it describes a transient state. One of the important results of new techniques to be described is that they enable us to ascertain for several enzyme systems whether or not K_m approximates to k_{-1}/k_1.

The study of enzyme reactions has as its ultimate aim a complete chemical explanation of the interaction of substrate with enzyme and of the subsequent reaction sequence that results in regeneration of free enzyme and final products.

This involves first the identification of the active groups on the enzyme and secondly a study of reaction mechanisms. In the case of enzymes with prosthetic groups it is relatively easy to ascertain the catalytically active site; in the case of pure proteins, however, one normally has to draw conclusions from circumstantial evidence. The number of different reactive side chains in the amino acids which form protein molecules is not very large; they are usually known from chemical analysis, and they can be identified in any particular enzyme system by correlating their known reactivities and ion association constants with inhibition studies [2, 3].

Both for the identification of groups of enzymes and for the elucidation of the mechanism of the reactions between enzymes and substrates one has to study the overall reactions under a variety of conditions with a number of different substrates, and for this purpose to devise methods which will reveal details of the kinetics of the reaction. The reaction between an enzyme molecule and a complex substrate molecule proceeds by way of a number of kinetically distinguishable steps. The overall rate constant k may characterize one particular step if this is very much slower than any of the others. In many cases, however, two or more steps have rates of the same order of magnitude resulting in an overall rate defined by

$$\frac{1}{k} = \frac{1}{k_2} + \frac{1}{k_3} + \dots \frac{1}{k_n} \quad \dots (3)$$

The rate constant k_1 of the formation of the initial enzyme-substrate compound is omitted from this relationship for the following reason. We can distinguish between the initial combination of enzyme and substrate, which follows second-order kinetics, depending on both enzyme and substrate concentrations, and all subsequent reactions of the enzyme-substrate compound, which follow first-order kinetics. This makes it possible to neglect k_1 when the substrate concentration is very high and, as will be shown, also to determine k_1 when the substrate concentration is very low. In many cases the overall rate constant of an enzyme reaction—and its dependence on pH, temperature, solvent composition, and modification of the substrate—does not characterize any one reaction step but is determined by two or more. In formulating reaction schemes for mechanisms and kinetic equations for the consecutive reactions, only such steps as have been experimentally distinguished should be taken into consideration.

Many very general schemes for the kinetics of enzyme reactions taking place under varied conditions and with hypothetical mechanisms have been reviewed during the last few years. We shall here describe a variety of new techniques for following the rates of enzyme reactions continuously, without sampling and over periods ranging from a few milliseconds to several minutes: these techniques have proved useful for the identification of specific steps. Techniques for studying such fast reactions are needed because the initial combination between enzyme and substrate is very rapid, and any intermediate enzyme-substrate compounds are therefore very short-lived.

Two distinct methods have been developed for the study of intermediate steps in enzyme reactions. First there is the method of 'observable intermediates', originally applied by B. Chance [4] to a number of enzyme systems having prosthetic groups or coenzymes whose absorption spectra change at some specific stage of the reaction sequence. The same principle is involved in the study of reactions of pure-protein enzymes with substrates whose spectra change during the course of the reaction. A second method for the kinetic analysis of intermediate steps was recently developed by the author [5]; this involves study of the initial acceleration of the rate of formation of the final products of enzyme reactions. When the steady rate of enzyme reactions is measured over periods of minutes, all intermediates have reached their steady-state concentration by the time of the first measurement. If, however, measurements are taken during the first few milliseconds of the reaction, the rate of appearance of the observed product increases until the concentration of enzyme-substrate compound reaches this steady state. The rate of the initial enzyme-substrate combination, as well as the rate of formation of other intermediate enzyme-substrate compounds, can be calculated from equations derived [5] for a number of special cases of initial acceleration phenomena.

FAST-REACTION METHODS

Each of the fast-reaction techniques described here was originally developed to solve one particular problem. Although most of them have found wider applications, the principles involved are best illustrated by reference to the system for which they were originally devised.

Most techniques for studies of rapid reactions in solutions are based on developments of the continuous-flow methods of H. Hartridge and F. J. W. Roughton [6]. This procedure consists of passing
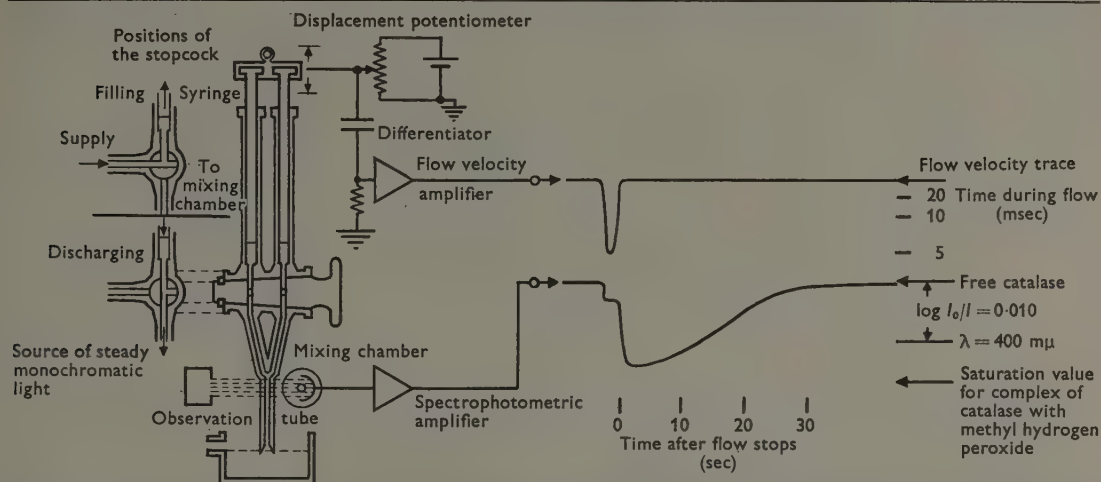
FIGURE I – *Diagram of apparatus for the accelerated- and stopped-flow methods of studying fast chemical reactions. At the right are shown typical experimental data for the formation and decomposition, in the presence of ethanol, of the complex formed between catalase and methyl hydrogen peroxide. (After B. Chance [9].)*

solutions of the two reactants, from separate containers, through a mixing chamber into an observation tube. If the flow of the mixed solutions in the observation tube is controlled at a known and steady rate, and the state of the reaction is observed in the tube at various distances from the mixing chamber, the reaction velocity can be calculated. The technique can be modified to meet particular circumstances by varying both the nature of the flow and the method of observation. So far as flow is concerned there are three major modifications:

1. Continuous-flow techniques, involving observations as described above.

2. Accelerated-flow techniques, involving observation at one point at varying flow speeds so that the time between mixing and reaching the point of observation is varied.

3. Stopped-flow techniques, involving observation in a chamber, immediately adjacent to the mixing chamber, after very rapid flow has been suddenly arrested.

A number of methods of observation have been employed, choice depending on their suitability for giving a continuous and rapid record of changes in the concentrations of particular reactants or products. The methods most widely applicable are photometric (spectrophotometric and fluorometric); potentiometric (measurements of pH and oxidation-reduction); and thermal.

Continuous-flow techniques, first employed [6] for kinetic studies of various reactions of haemoglobin, are not generally suitable for observations on enzyme systems because of the large quantities of materials, of the order of a litre of solution of each reactant, needed. The accelerated- and stopped-flow techniques, however, enable one to carry out a whole investigation on a few millilitres of reactant solutions.

CHANCE'S ACCELERATED- AND
STOPPED-FLOW METHODS

The spectrophotometric observation of the course of reactions in stopped-flow procedures has so far been the most useful method for the study of enzyme systems. The method involves driving the two reacting solutions from syringes into a mixing chamber and thence to the observation chamber; attached to the outflow from this chamber is a third syringe, the piston of which has just enough freedom of movement to allow a fraction of a millilitre to pass through the chamber before the flow of liquid is suddenly arrested. The degree of transmission of light of a selected wavelength is recorded when the flow of liquid has stopped. This procedure can give information about the change of concentration of reactants or products from 2 or 3 milliseconds after mixing. As originally designed by Chance (figure 1) the apparatus was used with a free outflow, without any stopping syringe: it could thus be used for combined accelerated- and stopped-flow experiments. The use of the method can be exemplified

by measurement of the rate of combination of the haemenzyme catalase with its substrate, methyl hydrogen peroxide, in the presence of ethanol. Although some side reactions take place, the principal products are methyl alcohol, acetaldehyde, and water, and to a first approximation the reaction can be described by:

$$CH_3OOH + C_2H_5OH + catalase$$
$$\rightleftharpoons CH_3OOH\text{-}catalase + C_2H_5OH$$
$$\rightarrow CH_3OH + CH_3C\!\!\diagup\!\!\!\!\!\diagdown\substack{O\\H} + H_2O$$
$$+ catalase \qquad \ldots (4)$$
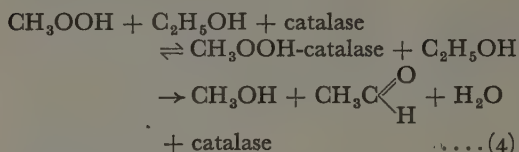
Catalase has a strong absorption band at 4000 Å; this absorption is approximately halved when the enzyme-substrate compound with methyl hydrogen peroxide is formed. Figure 1 shows the flow velocity (as milliseconds elapsed between mixing and observation) and the change in light absorption: two phases of this record require separate interpretation. Firstly, during the period of accelerated flow, data can be obtained for calculating the rate of the rapid combination of catalase with peroxide to form the enzyme-substrate compound. Secondly, after flow was arrested, a phase of slower reaction is recorded; as the substrate is exhausted, progressively less enzyme is present in the combined form. From this second record further data about the enzyme-substrate dissociation constant can be evaluated. The kinetic equations and a wide range of experimental results have recently been reviewed [7].

An ingenious form of rapid-reaction spectrophotometry has been used by H. Theorell and B. Chance [8] to study some of the steps in the reactions of liver alcohol dehydrogenase (ADH). The course of this reaction can be followed by observation of the changes in the spectrum of the coenzyme diphosphopyridine nucleotide (DPN), which is required for the reaction:

$$ADH + DPNH + CH_3CHO + H^+$$

Enzyme .   Reduced
coenzyme

$$\rightleftharpoons ADH + DPN^+ + C_2H_5OH$$

Oxidized
coenzyme
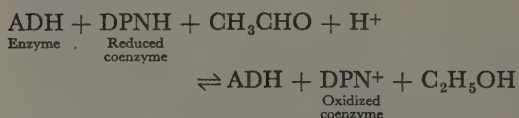
The difficulty of measuring the small change in light absorption resulting from the formation of the enzyme-coenzyme complex (ADH-DPNH) and in that resulting from oxidation of DPNH to DPN$^+$ was overcome in the following manner. The absorption of free DPNH is the same at both 3280 Å and 3540 Å, but the maximum change in molar extinction due to the addition of ADH

occurs near 3540 Å; furthermore, free DPNH and DPNH bound to ADH have identical molar extinction coefficients at 3280 Å. Chance [9] has designed an apparatus in which the light absorption can be measured at two or more wavelengths simultaneously: this is done by chopping each light beam at different frequencies. The output of the photocell is amplified in a circuit which can either record separately the changes in optical density at each wavelength or measure the difference of light absorption at two wavelengths. For the above investigation Theorell and Chance recorded the difference between light absorption at 3280 Å and 3540 Å, as well as the total light absorption at 3280 Å. In this way they obtained information about both the rate of formation of the ADH-DPNH complex and the rate of oxidation of DPNH to DPN$^+$, enabling them to interpret the kinetics of this enzyme system.

The necessity for economy in the valuable biochemical preparations used required the design of small observation chambers with an optical path of 1–2 mm. Furthermore, to follow most enzyme reactions it is necessary to detect either very small changes in molar extinction in solutions of low enzyme concentration or equivalent changes in the molarity of the coenzyme or substrate. This demanded the development of very sensitive spectrophotometric equipment. Strong monochromatic light sources are often necessary to detect changes within a narrow absorption band. Sensitive photomultipliers and stable amplifying and recording equipment with rapid response are required to measure changes in the intensity of the transmitted light. Chance has developed these various components of flow spectrophotometers to the highest level so far achieved, and his apparatus is extremely versatile. For certain specialized purposes, however, a simpler stopped-flow apparatus designed by Q. H. Gibson [10] is proving very useful.

GIBSON'S STOPPED-FLOW APPARATUS

This apparatus was originally developed for studies of the initial rate of combination of haemoglobin with oxygen. In its present form it is suitable only for spectroscopic observation with visible light: filters are used to select the particular wavelength of light required to detect changes in the concentrations of reactants or products. An original feature of the apparatus is the piston used for suddenly arresting the flow of the reactants. This device decreases the stopping time to about 1 millisecond and thus permits the study
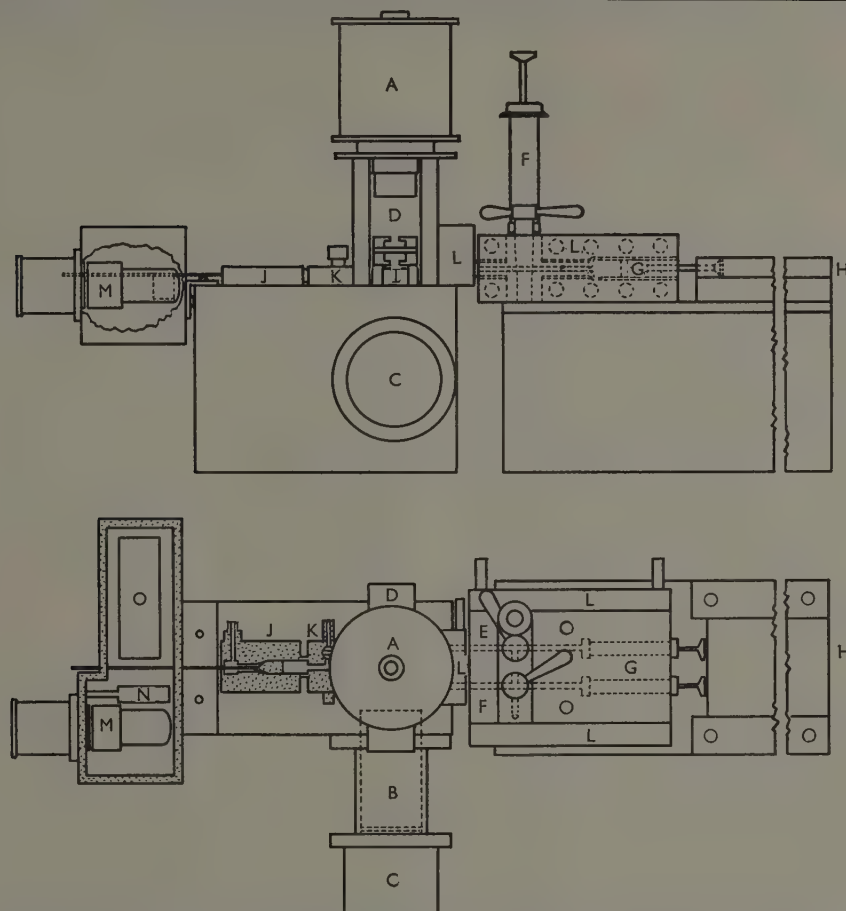
FIGURE 2 – *Elevation and plan of stopped-flow apparatus, after Q. H. Gibson* [10]. *Key: A, lamphouse; B, C, photo-multiplier and housing; D, filter carriers; E, F, 10 ml storage syringes; G, 2 ml syringes for driving solution from E and F into mixing chamber under lamphouse and filter carriers; H, block, running in V-guides, for driving pistons of syringes; I, mixing chamber; J, flow-stopping device; K, outflow tap; L, steel block through which water can be circulated to maintain constant temperature; M, N, O, apparatus for recording flow.*

of reactions with half-lives ranging from about 2 milliseconds upwards. Figure 2 shows the whole equipment, with the exception of the cathode-ray oscilloscope that is used for recording changes in light absorption by measuring the output of the photomultiplier (B).

The author and his colleagues [5, 11] have made extensive use of the Gibson apparatus in a variety of studies on the mechanism of enzyme-catalysed hydrolyses. To study the initial accelerations of ester hydrolyses a method has been adapted [12] for following changes in H^+ ion concentration spectrophotometrically by the use of indicators. Nitrophenyl esters have been used as substrates for hydrolytic enzymes, and it has been found possible to distinguish spectroscopically between different steps in the reactions between enzyme and substrate.

Figure 3 shows the record of measurements of changes in H^+ ion concentration during hydrolysis of benzoyl-L-arginine ethyl ester (BAEE) catalysed by trypsin or ficin in the presence of $10^{-3}M$ *p*-nitrophenol at *p*H 7·0:

$$BAEE + H_2O \underset{\text{trypsin}}{\overset{\text{ficin}}{\rightleftharpoons}} BA^- + H^+ + C_2H_5OH$$

In the reaction with trypsin the initial rate of formation of the enzyme-substrate compound is very rapid ($k_1 > 5 \times 10^6 M^{-1} sec^{-1}$), and even at very low substrate concentrations a steady state is reached within a few milliseconds. For the ficin-catalysed reaction the initial reaction is much
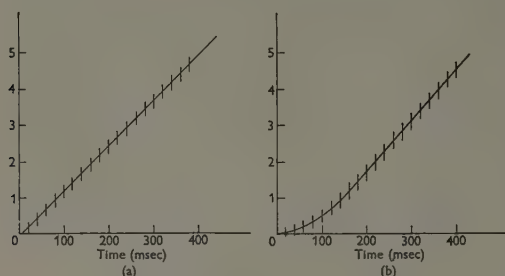
FIGURE 3 – *Oscilloscope traces showing changes in indicator colour during initial phase of enzyme-catalysed ester hydrolysis. (a) Trypsin-catalysed hydrolysis of benzoyl-L-arginine ethyl ester (enzyme, 10^{-6} molar; substrate, 4×10^{-5} molar). (b) Ficin-catalysed hydrolysis of same ester (enzyme, 10^{-4} molar; substrate 10^{-2} molar). (From H. Gutfreund [5]). The ordinates represent optical density changes, in arbitrary units.*

slower ($k_1 = 5 \times 10^2 M^{-1}sec^{-1}$), and it is possible to observe acceleration of the rate of appearance of products before the establishment of a steady state. Methods for evaluating rate constants from studies of the initial acceleration have been described in some detail [13].

The enzyme-catalysed hydrolysis of nitrophenyl esters (acetates or phosphates according to the enzyme) is a reaction very suitable for analysis of different steps in hydrolytic and transfer processes. H. Gutfreund and J. M. Sturtevant [11] followed the rate of liberation of nitrophenol and of acetate during the initial phase of reactions of chymo-trypsin, and were able to show that a three-step mechanism is necessary, and sufficient, to explain experimental results observed with a large variety of substrates. For different substrates, however, either the second or third step or a combination of the two determines the rate. The first step is a rapid adsorption; the second involves formation of an enzyme-acyl compound, with concomitant liberation of the basic part of the substrate; and the third is hydrolysis of this enzyme-acyl compound. Experimental evidence indicates that the enzyme is acylated at a serine hydroxyl group that interacts with one of the imidazole groups on the enzyme surface. Similar methods are being applied by the author to a study of a number of enzyme-catalysed reactions.

THE FLUORESCENCE METHOD

H. Theorell and A. P. Nygaard [14] found that fluorescence measurements were up to a thousand times more sensitive than spectrophotometry for the study of some dissociation reactions of enzymes with coenzymes. When flavine mononucleotide be-

comes attached to protein to form yellow enzyme, the fluorescence disappears. The forward reaction ($k_1 \simeq 10^5 M^{-1}sec^{-1}$) was found to be second-order, while the dissociation reaction ($k_{-1} \simeq 10^{-3}sec^{-1}$) is first-order. Accurate constants were obtained under a wide variety of conditions, enabling deductions to be made about the mode of enzyme-coenzyme combination.

Theorell [15] also applied the fluorescence method to further studies of the alcohol dehydrogenase diphosphopyridine nucleotide system, which has already been mentioned (p. 220). DPNH fluoresces with the same intensity whether it is free or bound to ADH, but DPN does not fluoresce. With the fluorescence method Theorell could carry out experiments in very dilute solutions ($10^{-6}M$), and combination of such measurements with those obtained spectrophotometrically gave much further information about the sequence of events during the reversible reaction previously mentioned.

CALORIMETRIC STUDIES OF ENZYME REACTIONS

Since there is always some heat change during a chemical reaction, calorimetry is in principle the most general method for obtaining a continuous record for the calculation of kinetic data. Since many enzyme reactions are accompanied by changes in the state of ionization of the reactants, a suitable choice of buffers can result in large heat changes, and experiments using different buffers help to distinguish between ionic and non-ionic steps in the reaction.

Accurate thermal measurements on a number of enzyme-catalysed hydrolyses have been reported during the last few years by Sturtevant [16]. These were reactions with half-lives of a few minutes, and they were characteristic of the steady-state velocity only. Such measurements are of great value; apart from giving thermal information about the reaction, they give a continuous plot and are so sensitive that rate data can be obtained when the concentration of the substrate is apparently constant.

Rapid-reaction techniques using temperature changes to follow the rates of reactions with half-lives of much less than a minute have not so far been applied to enzyme systems. The continuous-flow thermal method which has so far proved successful is too costly in enzyme, and a stopped-flow calorimeter of sufficient sensitivity and rapidity to overcome this drawback is only now in course of development.

MISCELLANEOUS METHODS AND
FURTHER DEVELOPMENTS

Several other modifications of the rapid-reaction techniques described here have been developed, and although they have not yet been applied to studies of isolated enzyme reactions they are likely to prove useful for this purpose in the near future. Chance [17] has been able simultaneously to record a number of physical properties (spectrum, oxygen tension, pH) during respiratory processes in various biological systems, and has overcome difficulties presented by the measurement of small spectral shifts which occur during oxidation in cytochrome systems in turbid suspensions.

Gibson [18] has shown how flash photolysis can be used for the study of very rapid reactions between haemoglobin and oxygen or carbon monoxide. If a carboxyhaemoglobin solution is exposed to the light from a flash-discharge tube, decomposition into haemoglobin and carbon monoxide occurs. The recombination of haemoglobin with either carbon monoxide or oxygen in the solution can be followed after the flash by conventional spectrophotometric methods. Chance [17] has employed photochemical initiation methods: such procedures permit the study of much faster reactions than can be investigated by the flow methods, since the limitation imposed by the finite rate of mixing of two solutions is removed.

So far as the future is concerned, the greatest advances in kinetic studies of reactions catalysed by isolated enzymes are likely to come from a combination of the methods described above. By observations at different wavelengths, and with instruments measuring different physical quantities, a single reaction can be investigated in several ways and the complex sequence of chemical events which comprise the reaction as a whole can be mapped out.

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example, the electron affinity of the OH radical has been measured [4].

Some of the most interesting work on high-temperature equilibria is that concerned with the gaseous species that are in equilibrium above solids having high melting points, particularly inorganic oxides and salts. These species are often very numerous and sometimes rather unexpected. For example, above barium oxide the gaseous molecules Ba_2O, Ba_2O_2, BaO, and Ba_2O_3 have been observed [5], and all the alkali hydroxides appear as stable gaseous molecules. L. Brewer [6] has found that, in the gas phase, cuprous chloride exists mainly in the form of the triple polymer $(CuCl)_3$, which has been shown to have a puckered-ring structure.

One example must suffice to illustrate some of the difficulties of quantitative thermochemistry at high temperatures. The example is a particularly important one—the determination of the latent heat of sublimation of carbon, or the energy required to separate one gram of carbon atoms from graphite. The standard method of determining such a quantity is to measure the vapour pressure of the material over a range of temperatures and to apply the Clausius-Clapeyron equation. In the case of carbon, however, where the sublimation pressures at workable temperatures are very small, the most convenient procedure is to measure the rate of effusion of carbon vapour through a small hole of known size in a furnace containing solid carbon at a high temperature. This experiment has been performed many times, in a number of laboratories, but with widely differing results. Published values for the latent heat of sublimation have ranged between 110 and 190 kcal/gram atom, and even two or three years ago the correct value was a matter for speculation. A different method of measurement, based on spectroscopic determinations of the dissociation energy of molecules such as carbon monoxide, served only to make the problem more intriguing, for they gave a number of apparently very accurate values for the latent heat covering as wide a range as those given by the thermal methods. It was, however, known that only one of these values could be correct, so that no more than a reasonably accurate measurement by some other method would be sufficient to decide which was right.

One of the main troubles of deducing the latent heat of sublimation from vapour pressure measurements was that most substances are more volatile than carbon, so that impurities, even in minute amounts, could invalidate the results. In the effusion method there were troubles concerned with the size of the hole through which the vapour effused: the hole has to be large enough to allow the experiment to be completed in a reasonable time, yet small enough to ensure that true solid-vapour equilibrium is established. Perhaps the most serious difficulty is one that was not really appreciated until relatively late in the history of the problem—that the particles leaving the carbon surface might not all be single atoms, so that the measured latent heat refers to equilibrium with some gaseous species other than carbon atoms. It was known that the diatomic molecule C_2 was stable, but there was good evidence that the contribution made by this molecule was small. Only very recently had C_3 been discovered spectroscopically, and there was no reason to suppose that this molecule was of any importance in the vapour at equilibrium.

The problem was ultimately solved by the mass spectrograph, and it seems certain that this instrument will in future play a predominant part in research on high-temperature equilibria. It overcomes all the difficulties mentioned above, since very small amounts of gas can be estimated and each species can be separately identified. When the technique was applied to the problem of the latent heat of sublimation of carbon by W. A. Chupka and M. G. Inghram [7] and by R. E. Honig [8] the problem was seen to be more complex than had previously been apparent. Not only was C_3 found to be an important constituent of the vapour in addition to C and C_2, but C_5 was also present; in addition there were appreciable amounts of negative carbon ions ranging from C^- to C_8^-. Study of the variation of the relative amounts of these species with temperature led to the evaluation of their heats of formation as well as to the latent heat of sublimation of carbon to atoms, L_c. Subsequent work has confirmed these experiments and established the value of L_c at 25° C as 170·89 ± 0·5 kcal/gram atom, thus resolving the outstanding thermochemical problem of the decade.

HIGH-TEMPERATURE KINETICS

The study of high-temperature kinetics is necessarily the study of fast reactions, although the converse is not true, because very many reactions are extremely fast at normal temperatures. The rate of a reaction is usually well represented by the equation

$$\text{Rate} = Ae^{-E/RT}$$

when E is an energy of activation, R is the gas constant, and A is a frequency factor which varies little with temperature. As the temperature is raised, the frequency factor assumes increasing importance relative to the activation-energy term. As the rate increases, there comes a point where we can no longer discuss the mechanism in these familiar terms, which are based on the concept of an equilibrium distribution of energy between the various motions of the molecules, because the rate of transfer of energy itself becomes important. The study of very fast reactions and of energy transfer are therefore two aspects of reaction kinetics which become particularly significant at high temperatures; in addition, the properties of electronically excited states may become important.

Experimentally, the outstanding problem to be faced is that of raising the temperature of the system quickly enough to make significant rate measurements possible. If this can be done, a study of the reaction is usually possible by modern electronic techniques, even if the time of reaction is only a few microseconds. But if the reaction itself is of such short duration it is obviously essential that the temperature rise be brought about in an even shorter interval of time; moreover, this must be done homogeneously throughout the material being investigated. Suppose, for example, that we wish to study the kinetics of thermal decomposition of ethane into ethylene and hydrogen at 1500° C, at which temperature the half-time of decomposition is one-millionth of a second. At 1000° C the half-time of reaction is one three-hundredth of a second, so that if we remain at 1000° C for as long as this, most of our material will have reacted before the experiment at 1500° C even begins. The method which is usually applied to slower gas reactions—that of admitting the gases to a vessel heated to the required temperature —would be quite useless for an experiment of this kind, since the observed rate of decomposition would be determined by the rate of thermal diffusion rather than by that of chemical reaction. Flow methods are sometimes useful, particularly in the study of flames, but the interpretation of such systems is rarely possible because of the complex diffusion phenomena associated with them.

The problem therefore resolves itself into one of raising the temperature of the gas, independently of its container, very rapidly and homogeneously. Two main methods fulfil these conditions—rapid adiabatic compression, particularly the extreme form of this, in which shock waves are utilized, and irradiation, the most useful form

of which is a short flash of visible or ultra-violet light. The electric arc is also a powerful and very simple method, but it is less useful for kinetic studies because of the uneven distribution of temperature within it.

Shock waves have been applied only very recently in investigating chemical problems. The principle is simple. When a gas is suddenly compressed it gains some heat; if the pressure is applied very rapidly, as may happen in an explosion, a high proportion of the mechanical energy is converted into heat. In the laboratory the shock can be produced in a very simple manner by bursting a diaphragm separating two parts of a tube containing gases at very different pressures. Temperatures of many thousands of degrees centigrade can be so attained, and, equally important, they can be produced quite uniformly throughout the gas in an extremely short time. The shock front is very sharp, because it heats the gas and so increases the velocity of sound in the gas behind it; the result is that the wave tends to pile up on itself, giving a shock front only a few molecules thick. Furthermore, the speed of the shock front may be so great that it passes two slits, one millimetre apart, in about one microsecond. If, by some optical method, we examine the gas as the shock front passes, it is quite possible to heat the gas to several thousand degrees and begin measurements of reactions in it within the space of a few microseconds.

The shock tube has so far been applied only to a few chemical kinetic problems, the main ones being the dissociation of nitrogen oxides [9] and of halogen molecules into atoms [9, 10]. The latter study was exceptional in kinetic work because the rate constant can also be derived from flash photolysis studies of the reverse (recombination) reaction at low temperatures. The two methods provide an expression for the rate constant of dissociation of bromine over a temperature range corresponding to a change in the rate by a factor of 10^{27}. The shock technique promises to be one of the most powerful methods for the study of high-temperature gas kinetics.

The second method for producing a rapid temperature rise utilizes the energy of a light flash of a few microseconds' duration, and has not yet been fully investigated specifically for high-temperature research. It has been much used for producing rapid dissociation or electronic excitation [11], but in these applications one is usually concerned with keeping the system nearly isothermal, which can be accomplished by working

with excess of inert gas. The course of the subsequent reactions is, as usual, studied by optical and electronic methods. If the inert gas is omitted and the substance is an efficient absorber of light, a very rapid temperature rise results, because all the absorbed energy that is not used in chemical reactions will be dissipated as heat. Energies of the order of 100 kcal/mole may be absorbed, and the corresponding temperature rise may be very considerable: for example, if the specific heat of the gas remained constant at 5 cal/mole, a temperature of about 20 000° C would be attained. As usual, the gas dissociation greatly reduces this temperature, but in the first stages the rate of heating is nevertheless very high. The method has the disadvantage that it is restricted to gases which absorb light and that most of these—though not all—dissociate photochemically. It has the advantage, however, that the temperature rise may be produced fairly homogeneously in a long path of gas; reaction vessels one metre long are commonly used, and consequently absorption spectra have been observed of intermediates that cannot be detected by other methods. The main application of flash-radiation heating has so far been to the homogeneous initiation of explosion; in this case a long reaction zone has the advantage of making possible the detection and estimation of the intermediates as a function of time during the explosive reaction. It has been applied to high-temperature kinetic problems of practical importance, such as the mechanisms of carbon formation and of anti-knock action in internal combustion engines.

'TEMPERATURE' IN FAST REACTIONS

Some of the most interesting problems in fast-reaction kinetics are associated with the fact that the temperature itself cannot always be clearly defined. In a slower reaction, even though the gases are not in chemical equilibrium, the molecules are in thermal equilibrium with each other, and the energy is distributed among the various degrees of freedom in a well-defined manner. This Boltzmann distribution of energy forms the basis of all the usual formulations of theories of reaction rate.

In a typical fast reaction—such as the combustion reaction in a flame—the gases are heated, undergo a most complex series of chemical changes, and leave the reaction zone as burned gases in a time which may be less than one-thousandth of a second. In such circumstances it is not surprising if thermal equilibrium no longer obtains at all stages of reaction. The absence of thermal equilibrium is shown most clearly when the 'temperature' of the reaction zone is measured by different methods. All the methods agree fairly well when applied to the burned gases above the reaction zone, but they may differ widely in respect of the reaction zone itself. If a method is used that depends on the degree of electronic excitation—as, for example, does the commonly used sodium line reversal method—we may find that the measured temperature depends not only on the element used but even on its particular electronic levels. Measured values as high as 8000° C have been found, using the reversal of iron lines, in flames whose theoretical maximum temperature was only 1700° C. Matters are little better when the temperatures associated with other degrees of freedom are measured. The 'rotational temperature', estimated from the intensity distribution among rotational lines in molecules like OH and C_2, may be as high as 10 000° C, and anomalies are also found in vibrational intensities. Even 'translational temperatures', which might reasonably be considered as true temperatures, seem to be anomalously high in some cases when measured from the Doppler width of spectral lines. Some flames, for example those of H_2 and CO, do not show any great anomalies, while others, for example hydrocarbon flames, show very large ones [12].

The anomalies are almost certainly caused by a breakdown of the Maxwell-Boltzmann distribution in rapidly reacting gases, and are to be expected fairly generally throughout high-temperature kinetics. The difference in temperatures determined by various methods tells us, in no uncertain manner, that simple rate-equations containing a single energy term and a single temperature value are not going to be sufficient. The problems of energy transfer between molecules and their various degrees of freedom, and of reactivity of molecules as a function not only of energy content but of its distribution within the molecule, present a field of general theoretical importance which is particularly relevant to high-temperature reactions.

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Towards a unity of knowledge

The editorial in our April issue, urging the need for a synthesis of scientific and humane studies, has been favourably received and widely quoted. The interest of those whose primary concern is with the humanities is particularly welcome, and for this reason we are glad to publish the following joint letter from Lord Samuel, Lord Halsbury, and Sir David Ross.

Sir,

We have been greatly interested to read the editorial article in your April number entitled 'Towards a unity of knowledge'. This impressive plea for a closer association between science and the humanities, appearing in a periodical with the status and influence of ENDEAVOUR, was very welcome to an organization such as The Royal Institute of Philosophy, one of whose chief objects is to try to bring philosophy into closer relation with the main currents of practical life. The point closely touches the present discussion of the right lines for the development of the national system of education in Britain.

The philosophers who in the latter part of the 17th century founded the Royal Society were soon obliged, by the rapid accumulation of knowledge about Nature, to departmentalize their work. In later generations they took the new name of scientist and separated their studies from the older branches of philosophy—metaphysics, ethics, and logic. This divergence has since continually widened, until we have become aware in the present generation of a gap, causing a lack of understanding and of any effective measure of association, that is having harmful results, not only in the sphere of education but also in ethics and in politics, both national and international.

But, as you say, 'it does not seem that the gap is unbridgeable'. Within science itself, you point out, a process of unification is going on that might have seemed difficult a few decades ago, between pure and applied science, and again between physics and chemistry on the one hand and biology on the other. You suggest that, without either side sacrificing the specialization that is essential to efficiency, a synthesis might also be achieved, at a deeper level, between science itself and the humanities.

This is also our conviction. There is a wide province where the two overlap, particularly in theoretical physics and empirical philosophy, that is of great interest at the present time. And in general, in the universities and at all levels of education, it is becoming increasingly plain that science and philosophy cannot continue to go on regardless of each other's activities, sometimes, it would seem, hardly on speaking terms with one another. Every philosopher should understand the outlook and the conclusions of science, every scientist have an appreciation of the humanities; and every well educated man, while tending no doubt to a greater interest in the one or the other, should have had the opportunity to gain some knowledge of both.

When, therefore, you give prominence to such a plea, and show that from the side of science there is now a marked trend towards such a synthesis, we think it is right not to leave this initiative without response from the side of philosophy, but to say that a similar approximation is also to be seen among many present-day philosophers, and that there is reason to hope that it will continue and develop.

The Royal Institute
of Philosophy
London

SAMUEL
President

HALSBURY
Vice-President

W. D. Ross
Chairman of the Council

Book reviews

THE EARTH AND THE HEAVENS

Encyclopédie Française. *Vol. III*, Le ciel et la terre, *edited by A. Danjon, P. Pruvost, J. Blache. Pp. 452. Librairie Larousse, Paris. 1956. Fcs. 7450 net.*

This work, to which 36 authors, all of whom are specialists in their subjects, have contributed, is divided into two parts, as indicated by its title. The first part comprises four sections dealing respectively with the solar system, the Sun and stars, the galaxies, and problems of evolution. The second and larger part is concerned solely with the Earth, considered from different aspects. The first section of this latter part deals with the problems of geophysics: meteorology, the aurora and airglow, the ionosphere, geomagnetism, tides, gravimetry and isostasy, seismology, and the interior of the Earth. The second section is geological and discusses the origin of the surface rocks, the transformations they have undergone, past geological history, and the information that can be derived about the evolution of the Earth. The third section is concerned with the Earth as it exists at present; its atmosphere and climates, the oceans, lakes, rivers and underground waters, and the moulding of the surface features.

The aim throughout the work has been to emphasize recent advances in knowledge and to present current theories and ideas, relating them to facts and theories that have been well established and are generally accepted, but without any detailed exposition. The volume therefore forms a valuable work of reference. The binding is in the loose-leaf form so that revised or new pages can be inserted; it is proposed to issue such pages from time to time, as new material becomes available. The illustrations are excellent and well selected; the large majority of those in the first part are reproduced from photographs obtained at French observatories.

H. SPENCER JONES

WAVE MECHANICS

Mathematics and Wave Mechanics, *by R. H. Atkin. Pp. xv + 348. William Heinemann Ltd., London. 1957. 30s. net.*

Mr Atkin has written this book for Honours degree students in physics and chemistry, and it is clear that he is a mathematician thoroughly familiar with their needs. The scope is wider than the title might suggest, for not only are many aspects of the application of wave mechanics treated but some 200 pages cover most of the mathematical operations necessary in theoretical physics and chemistry.

The introductory chapters dealing with the more elementary concepts such as complex number theory and the evaluation of integrals tend inevitably to be unrelated, but this enables individual topics to be read with the minimum of reference to earlier pages. The purely mathematical chapters are concise and the worked examples included in the text are well chosen to illustrate and enlarge the theory.

The application of mathematics to physics is introduced by way of classical mechanics and electromagnetic theory. The results of experiments in the early twentieth century are then shown to give rise to special relativity and quantum mechanics. By this stage the reader should have become well acquainted with vector and matrix algebra. Numerous applications of wave mechanics range from the simple harmonic oscillator to Rutherford and Compton scattering, and there is a chapter devoted mainly to valency bonds.

The book is well produced and its price reasonable. W. R. MYERS

HYGROMETRY

Hygrometry, *by H. Spencer-Gregory and E. Rourke. Pp. xv + 254. Crosby Lockwood & Son Ltd., London. 1957. 36s. net.*

Humidity measurement is a factor of major importance in many industries, but the literature on the subject is widely scattered and there has been a need for a practical text-book for users of hygrometers. This book scarcely meets this need, since its emphasis is on detailed theory rather than on practical instruction.

The lay-out is rather muddled; for example, the introductory chapter occupies nearly one quarter of the book and includes much that would be more appropriate under the headings of the later chapters. There is, in consequence, frequent cross-referencing which could have been avoided by more careful planning.

Among the more useful chapters are those on the hair hygrometer and on the moisture content of highly compressed permanent gases. Another chapter gives psychrometer theory in great detail, but makes no mention of the recent work of J. L. Monteith. The effect of lag in hygrometers is discussed, but its practical application is not made very clear.

The book may have some academic interest, but the technologist seeking practical guidance will probably be disappointed, especially on finding that only about half the authors quoted are included in the bibliography.

F. J. SCRASE

TENSORS APPLIED TO CRYSTALS

Physical Properties of Crystals, *by J. F. Nye. Pp. xv + 322. Oxford University Press, London. 1957. 50s. net.*

Many properties of crystals may be represented mathematically by tensors, though some, such as surface properties, cannot. Although not concerned to explain particular crystal properties in terms of structure, this work will be of great help to those interested in the attempt to do so. Its backbone is a treatment of tensors which shows how they may be used as a common basis for interpreting many properties and the thermodynamic relations between them.

The mathematical treatment is reasonably simple, but the work is likely to make its greatest appeal to post-graduate students and research workers. Metallurgists, and those engaged in solid-state physics, will find a useful introduction to tensors and matrix algebra. A number of properties, thermal, electrical, mechanical, are treated individually, and a special chapter gives a unified treatment of the thermodynamics of these equilibrium properties. Transport properties are dealt with separately. Crystal optics includes happily a section on optical activity in crystals. H. M. POWELL

ORGANIC STRUCTURE

Introduction to Structure in Organic Chemistry, *by C. K. Ingold. Pp. vii + 200. G. Bell & Sons Ltd., London. 1956. 20s. net.*

In response to requests, Professor Ingold has reproduced, under the above title, the first four chapters of his larger treatise 'Structure and Mechanism in Organic Chemistry' which has now become a standard work of reference in the realm of physical organic chemistry. The four chapters of the present book are so comprehensive that they can hardly be considered as a mere 'introduction' to the subject.

The approach is essentially that of an organic chemist who needs to know about molecular structure in order to develop theories about chemical reactions. Thus after a short, fairly standard, introduction Ingold deals in his second chapter with interactions within and between molecules in terms of molecular polarization and molecular polarizability. This leads to a detailed explanation of the significance of inductive and mesomeric effects. The third chapter relates these concepts to physical measurements with aliphatic compounds and the fourth deals with aromatic character.

The book leaves one with a picture of tangible molecules of fairly definite geometrical shape with reasonably stable, though deformable, electronic constitutions. The picture is elucidated by experimental measurements and not just deduced by mathematical theory.

This treatment is just what the chemist requires and can comprehend.

W. A. WATERS

HETEROCYCLIC COMPOUNDS

Heterocyclic Compounds, *Vol. V, edited by Robert C. Elderfield. Pp. vi + 744. John Wiley & Sons Inc., New York; Chapman and Hall Ltd., London.* 1957. 160s. *net.*

This substantial book continues the high tradition of earlier volumes in this very valuable series. The eight chapters cover 1,3-dioxolane and derivatives (R. C. Elderfield and F. W. Short), pyrazoles and related compounds (T. L. Jacobs), indazoles (R. C. Elderfield), imidazoles and condensed imidazoles (E. S. Schipper and A. R. Day), oxazole and its derivatives (J. W. Cornforth), benzoxazoles and related systems (J. W. Cornforth), isoxazoles (R. A. Barnes), thiazoles and benzthiazoles (J. M. Sprague and A. H. Land). It is claimed that the major English and German-language periodicals have been covered up to the end of 1955. The pyrazoles (117 pages), the imidazoles (104 pages), the oxazoles (120 pages), and the thiazoles (239 pages) receive extremely full treatment.

It is a tribute to the uniformly high quality of the writing that these detailed and comprehensive chapters, though likely to be used mainly for reference purposes, are yet readable and stimulating. The generous use of formulae and the many footnote references (about 4000) make this book invaluable to the research worker. The formulae are occasionally awkward and there are

some errors; use should have been made of the simplifying Me and Et for functional methyl and ethyl groups and of Ph for phenyl. There are occasional unacceptable uses of arrow symbols. The cleavage of methylenedioxy groups by phosphorus pentachloride, followed by hydrolysis, is due to Barger (1908), rather than to German patents of 1915 and 1922. There is regrettably no author index, but the subject index is more comprehensive than those of the earlier volumes. W. BAKER

PETROCHEMICALS

The Chemistry of Petrochemicals, *by Marvin J. Astle. Pp. v + 267. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London.* 1956. 52s. *net.*

During the last two decades a revolution has occurred in the manufacture of organic chemicals, in that petroleum has taken first place among the sources of carbon compounds. The rate of increase is itself increasing and it is impossible to predict the point of equilibrium between supply and demand in the foreseeable future. Major products are a wide range of solvents, glycol for antifreeze, detergents, agricultural chemicals of various types, and a long series of resins, plastics, and elastomers. We may expect, and must welcome, a series of books on the topic of petrochemicals to keep pace with such a rapidly expanding subject.

The author of the present work has had detailed experience in the industry and is at the present time Professor of Chemistry at the Case Institute of Technology, Cleveland. He is thus unusually well qualified to speak with authority on both the theoretical and practical aspects.

The book covers the material remarkably well and has some claim to be regarded as a work of reference. Nevertheless there are some noticeable gaps, one example being the omission of any mention of the important insecticides made from *cyclo*pentadiene and its hexachloro-derivative. A good balance is maintained between the theoretical explanations and the summaries of actual conditions of reactions, this being a very valuable feature.

A high standard of accuracy is maintained but there are nevertheless a few fallings from grace. The spark that lit the polyethylene train was not an attempt to combine ethylene with benzene (p. 102) but with benzaldehyde. In the same section the emphasis in the description of the Ziegler catalyst is

wrongly distributed or there is misunderstanding; in either event it gives a wrong impression.

Though not perfect the book can be recommended both to students and to research workers in the field. The printing and presentation are good but the price is too high.   R. ROBINSON

BIOCHEMICAL VARIATION

Biochemical Individuality, *by R. J. Williams. Pp. xiii + 214. John Wiley & Sons Inc., New York; Chapman and Hall Ltd., London.* 1956. 46s. *net.*

The genetotrophic principle, as the author conceives it, is a broad one encompassing the whole of biology. It is stated that every individual organism possessing a distinctive genetic background has distinctive nutritional needs which must be fulfilled for optimal well-being. At the human level, the concept, even if true, is of little importance unless large variations in body chemistry can be demonstrated. This book gives a clear and concise account of these variations with reference, for example, to specific enzyme levels, endocrine activities, and nutritional needs. The reviewer is unaware of any similar attempt to bring together the available material on normal biochemical variation. The author outlines a substantial case in support of his conclusion that each human being possesses a highly distinctive body chemistry.

The author is convinced of the substantial truth of his general thesis but presents his ideas without dogmatism. The reader will find much that is original and the account is stimulating throughout. The ideas outlined have implications not only for biochemists and medical scientists but also for psychologists, anthropologists, and workers in the educational field.

The material is well arranged and printing, paper, and binding are excellent.   W. G. OVEREND

VIRUS SYMPOSIUM

The Nature of Viruses (Ciba Foundation Symposium), *edited by G. E. W. Wolstenholme and E. C. P. Miller. Pp. xii + 292. J. and A. Churchill Ltd., London.* 1957. 42s. *net.*

This Symposium was held in March 1955 with the title of 'The Biophysics and Biochemistry of Viruses' under the chairmanship of Sir Charles Harington. Many of the world's leading virologists took part and the informal discussions following each paper constitute one of

the important features of the book. The subjects dealt with are the fundamental aspects of virology and include, among others, the structure of virus particles, chemical studies, multiplication of viruses, and studies of cell infections by means of fluorescent antibody and the use of radioactive influenza virus.

The study of virology now embraces so many widely differing disciplines that one welcomes this opportunity for physicists and chemists to confer with biologists and so come to a closer understanding. Some of the results of the intensive research on the problem of virus during the last ten years are seen in this book. Crick and Watson discuss the general principles of virus structure with particular reference to the small plant viruses containing only protein and ribonucleic acid. This is followed by an interesting discussion by Robley C. Williams of the structure and sub-structure of viruses as seen under the electron microscope. This instrument alone is able to furnish morphological information about the individual virus particles by direct optical imagery. This discussion and the following one by Dr Franklin and her colleagues on X-ray diffraction studies, deal mostly with the structure of the tobacco mosaic virus particle. The work in California suggests that the ribonucleic acid (RNA) alone of the tobacco mosaic virus is infectious and raises the possibility of injecting RNA and DNA (deoxyribonucleic acid) directly into the cell to find out if these alone can start infection. Some of the practical results arising from this fundamental work on viruses are considered by Burnet in the general discussion. The purification of viruses may help in the production of vaccines to prevent virus infections in man. Furthermore, the most efficient vaccines are those with active avirulent strains of virus, rather than those with inactivated virus, and this work will help in the selection of suitable strains for this purpose.

Of two other major objectives one is the exploitation of the virus, as a comparatively simple system, in the understanding of protein synthesis. The other is the explanation of virulence, since this has a fundamental bearing upon the effects of the virus on the host. This was a most successful symposium and the book resulting from it is stimulating.

K. M. SMITH

MITOCHONDRIA

Symposia of the Society for Experimental Biology. No. X: Mitochondria and other Cytoplasmic Inclusions. Pp. 198. *Cambridge University Press, London.* 1957. 55s. *net.*

This series of papers reflects the worries and confusion that are the lot of those who work in the fascinating field of the optical and chemical properties of cell components. This is most marked in the case of the Golgi 'zone' or material, where alternate authors assert that it is 'real' and that it is an 'artefact'. Most cytologists probably realize the logical and technical difficulties involved in defining such concepts. Dr Novikoff, in a wise article, refers to the danger of study of particles 'torn by grinding devices from a cellular milieu selected during aeons of evolutionary time'. But this is almost the only reference in the book to the cell as part of a whole living system. Drs Dalton and Felix tell us that we should be satisfied that the Golgi component 'exists in freshly isolated cells and that it may be identified by its peculiar optical properties under these conditions'. The cell that they show is described as 'isolated in 4% NaCl containing 0·1% methylene blue'—no wonder the appearance was 'peculiar'.

The reader will learn more from the articles that deal with mitochondria. There are stimulating discussions of the appearance of these under different conditions, and of whether they show fundamentally different types of structure within any one cell. Discussion of the relationship between enzymic activity and the various particles appears sporadically. D. E. Green discusses the 'cyclophorase' system in relation to cellular organization. It is clear that we are not yet ready to discuss how the many isolated findings by electron-microscopists and biochemists are related to cell functioning as a whole.

Many of the articles are illustrated by good figures, but it is irritating to have to turn many pages to find the description of them. Many of them do not carry scales and one suspects that the magnifications given in round figures in the text must be incorrect.

J. Z. YOUNG

MAMMALS

The Life of Mammals, by *J. Z. Young.* Pp. xv + 820. *Oxford University Press, London.* 1957. 84s. *net.*

The most important point to make in any appraisal of this work is that it is not just another book on the structure and function of mammals. It is planned and written in terms of a concept, which may in itself not be new, that animals are self-controlling systems whose activities are devoted to the maintenance of a stable pattern. But so far as I know, no major synthesis has previously been attempted to interpret the now vast accumulation of facts in the fields of anatomy, physiology, embryology, ecology, and genetics, in terms of what is now also known of the principles and properties of machines that regulate themselves. It would be a complete mistake to conclude from this that the author has decided that animals are nothing more than servomotors. On the contrary, he has used this concept as a principle to be applied as far as it will go, which means as far as scientific evidence will allow, in order to understand better how animals live. They remain alive because they make the appropriate responses during development when they build themselves, and in adult life when they maintain themselves. They make use of the data provided by heredity, by the environment, and by a store of information which they have amassed (also called experience) and which they either keep to themselves as memory or communicate to fellow-members of their species by social contacts, and in the case of man to posterity by tradition whether oral or written. Finally, the self-regulating pattern is coded into the hereditary material of the genes for the succeeding generation.

It is by failure to make appropriate responses that organisms succumb to natural selection. It is by the reshuffle of genes that have undergone mutation that selection favours those types that are regulated to make the most appropriate responses to their environments (whether changed or not), and this is evolution. The interpretation of organisms in terms of the control mechanisms by which life is maintained is therefore applicable to all fields of biology, and provides a unifying concept in a field where descriptive and comparative methods have already produced numerous generalizations, and analysis has yielded innumerable principles of partial and restricted applicability. What Professor Young has been looking for is a language which describes the whole living organization. There will be time enough to know whether there are any aspects of that organization that resist integration in this system. Meanwhile he has provided a framework, as Darwin said of his own work, 'to guide our speculations'.

Special praise must be accorded to

the illustrations by Miss E. R. Turling-ton and Miss J. I. D. de Vere, and to the production of the volume by the Clarendon Press.   GAVIN DE BEER

THE RETICULO-ENDOTHELIAL SYSTEM

Physiopathology of the Reticulo-Endo-thelial System. A Symposium organized by The Council for International Organizations of Medical Sciences, *edited by B. N. Halpern, B. Benacerraf, and J. F. Delafresnaye. Pp. xii + 317. Blackwell Scientific Publications, Oxford. 1957. 45s. net.*

A volume devoted to the reticulo-endothelial system will always receive a warm welcome, since there is scarcely a corner of medicine into which this important concept does not intrude.

A graceful introduction by Vallery-Radot is followed by a useful, concise account by Policard of the morphology and physiology of the reticulo-histio-cytic cell, as he prefers to call it, and Sadron states the principles that are used to determine the shape and dimensions of globular proteins in solution.

Three main aspects of the reticulo-endothelial system are then discussed in some detail. In the first instance, the factors that influence the functional efficiency of the system form the subject of four interesting papers based upon methods for estimating the rate at which particles of various sizes are 'cleared' from the blood and englobed by reticulo-endothelial (R.E.) cells. Everything depends, of course, on the soundness of the claim that the particles favoured by each particular investigation behave as stated. They must preserve their individuality during the period of quantitation and show no tendency to stick together in clumps, as is admitted to happen so frequently in the pulmonary vessels, and removal must be strictly by way of R.E. cells. The reviewer finds it difficult to accept these assumptions light-heartedly, although several workers state quite definitely that nearly all of the introduced material can be accounted for in the liver and spleen. Granted these assumptions, many striking features emerge, such as the remarkable selective capacity of the liver for small amounts of particles, the dependence of phagocytosis on rate of flow of blood past the phagocytes, instances of preferential phagocytosis, and the avidity of the spleen for large particles.

The second group of papers is devoted to certain aspects of R.E. cell meta-bolism. Byers *et al.* suggest, with proper caution, that R.E. function is important in the normal disposal of chylomicron cholesterol and Vanotti gives a balanced discussion of the metabolism of iron. Miescher's account of the disposal of red blood corpuscles by the system is a model version of an exasperating, often muddled topic. Hahn and his colleagues describe their fascinating experiments on the production of cirrhosis and ascites by massive irradiation of the R.E. systems with radioactive gold colloids, and Nöller gives concisely much information on the storage capacity of the system and the way in which it can be modified by drugs.

The third aspect of the symposium brings us face to face with the most engaging question of medicine, the defence against infection. Miles summarizes his views on local defences and their relation to general R.E. defence; Halpern *et al.* apply their quantitative methods to experimental infection; Cruchaud and Tekul decide that cortisone modifies antibody distribution in an organism by increasing the proportion of cellular antibodies to circulating antibodies. Gell discusses the nature of some tissue hypersensitivity reactions and Doan discusses R.E. cells generally in relation to health and disease. We owe to Lewis Thomas a little masterpiece on the role of the reticulo-endothelial system in the reaction to endotoxins, which is a delight to read because of its clarity and provocative outlook.   G. R. CAMERON

DE MOTU CORDIS

Movement of the Heart and Blood in Animals. An anatomical essay by William Harvey, translated from the original Latin by Kenneth J. Franklin. Pp. xii + 209. Published for the Royal College of Physicians of London by Blackwell Scientific Publications, Oxford. 1957. 17s. 6d. net.

William Harvey died on 3rd June 1657, in his eightieth year. A tercentenary congress of those interested in him, in his work, and in its innumerable modern developments was held in London and at his birthplace, Folkestone. This translation of Harvey's great book *Exercitatio anatomica, De motu cordis et sanguinis in animalibus* was a highly appropriate presentation to the members of the Congress.

Harvey's text was first issued in Latin at Frankfurt am Main in 1628 by William Fitzer. The publication of this book was a landmark in science, since it both laid the foundations of modern experimental physiology and provided a firm mechanical basis for many hundreds of thousands of important clinical observations during the three following centuries.

The 1628 edition is of only some 72 pages. Both the Latin version and the English translation reproduced by Professor Franklin occupy about the same space. But Harvey himself had a quite conspicuously bad handwriting, and the 1628 text is a wretched piece of printer's workmanship, full of errata, some acknowledged by the printer himself. It has often been reproduced, both in facsimile and reprint, and has several times been translated. Professor Franklin, we think wisely, did not base his English version on the stately and scholarly edition issued by the Royal College of Physicians of London in 1766. His new English version undoubtedly excels in literary grace, and in exactness of rendering, any that has yet appeared. It will therefore automatically take its place as the standard version, for it is prepared not only with a high sense of scholarship and with accurate knowledge of its original, but also with the unique mastery that Professor Franklin possesses of the difficulties that presented themselves to Harvey and to the public that he was addressing.

All this makes us regret the more that this admirable effort is presented without any commentary and with no attempt to relate the history of Harvey's discovery. For such matters Professor Franklin is uniquely equipped. We can but hope that he will find the leisure to complete the task that he has begun in so masterly a fashion.
CHARLES SINGER

CROP PROTECTION

Plant Protection Conference 1956. Pp. xi + 315. Butterworths Scientific Publications, London. 1957. 50s. net.

Great improvements have been made during the past thirty years in the yields and quality of crops all over the world. The chemical control of pests, diseases and weeds, the breeding of plants resistant to attack, and better methods of nutrition and husbandry have all played a part. This book reports the proceedings of a Conference, attended by 200 scientists from 42 countries, convened by Plant Protection Ltd., to discuss the fundamental aspects and future trends of the new science of crop protection.

Sir Frank Engledow, in a stimulating

opening address, calls attention to the dependence of crop protection upon the basic sciences, and to the responsibilities of scientists in ensuring that its practice is built upon a sound foundation. The world aspects of the subject are ably reviewed by J. G. Knoll (Food and Agricultural Organization of the United Nations), who discusses the pests and diseases of international importance and the collaborative measures taken for their suppression. The problems arising in the breeding of plants resistant to attack are dealt with by W. F. Hanna (Ottawa), and the application of genetics in raising cotton resistant to blackarm disease is described by R. L. Knight. A valuable contribution on the physiology of immunity of plants is made by Professor Suchorukov (U.S.S.R.). The mechanisms of toxicity of fungicides and insecticides are examined by S. A. E. McCallan (U.S.A.), J. W. L. Beament, and J. T. Martin, while systemic compounds for pest, disease and weed control receive special attention from R. L. Metcalf (U.S.A.), E. Åberg (Sweden), V. J. Masten and J. Hočevar (Yugoslavia), and P. W. Brian. Assessments of hazards to operator and consumer of crop protection chemicals and of residual effects in soil are made by J. M. Barnes, R. Fabre and R. Truhaut (France), and F. J. D. Thomas (Australia). The mechanics of formation of spray droplets are discussed by R. P. Fraser and methods of spray application are described by Van den Muijzenburg (Holland) and R. C. Rainey.

Crop protection is expanding rapidly, and it is essential that, from time to time, inter-related aspects should be reviewed and placed in proper perspective. The book admirably fulfils this purpose. It contains a wealth of authoritative information, both in the formal papers and in the excellent discussions which are fully reported. Great credit is due to the organizers of the Conference in covering the subject on such a broad basis.   J. T. MARTIN

BRITISH INDUSTRIAL PROGRESS

Industry and Technical Progress, *by C. F. Carter and B. R. Williams. Pp. viii + 244. Oxford University Press, London. 1957. 25s.*

This report, written by two economists, contains the results of a most painstaking analysis of the factors influencing the application of science in British industry. But in spite of all the work that has gone to its compilation, it is a disappointing document, as it fails to give the bold and imaginative lead that it admits is so badly needed in many firms. One chapter is devoted to showing why it was inevitable that certain discoveries first made in Britain should have been developed elsewhere. Take the transistor. Would it not have been more helpful if we had been told of the very effective system of administration of research and development in the Bell Telephone Laboratories that helped so much in the development of the transistor and of much besides? What of Calder Hall, Britain's outstanding technical achievement? Why are we not told of the bold and unique way in which research was there tied in with the engineering effort, making its rapid progress possible?

Little is said about the role of the engineer on whose intuition and experience the successful application of research so largely depends. Greater productivity is one of the main aspects of technical progress, and there Work Study, developed so largely under the stimulus of an engineer, Sir Ewart Smith, is the sequel to Operational Research, a war product of scientific analysis.

The rather half-hearted assessment of the advantages of the presence of scientists on the Board, with its nicely balanced arguments, may have been valid in the past, and will no doubt be comforting to those who are suspicious of engineers and scientists at the policy-making level; but will it be equally true in the future, when in many firms their products ten years hence are unknown today?   HAROLD HARTLEY

HISTORY OF TECHNOLOGY

A History of Technology, *Vol. II. The Mediterranean Civilizations and the Middle Ages, edited by Charles Singer, E. J. Holmyard, A. R. Hall, and Trevor I. Williams. Pp. lvii + 802. Clarendon Press, Oxford. 1956. £8 8s. net.*

Volume II of this splendid work carries on the story of the development of western technology from *c.* 700 B.C. to *c.* A.D. 1500

It is a fascinating period of world history. It starts with the rise of the Greek city-state from the ruins of the Mycenaean culture. The famous philosophers of ancient Greece reached heights of intellect which were not surpassed for 2000 years; but they gave little encouragement to the mechanical arts which, wrote Xenophon, 'carry a social stigma and are rightly dishonoured in our cities'. So in the end Greece was overrun by the more practical Romans, in spite of the exertions of Archimedes, who is described in this volume as 'the greatest military engineer of all antiquity'.

The Romans were an intensely practical nation. They adopted and extended the techniques of the conquered nations of the East, and spread them over the West. 'Their practical knowledge of machinery was not surpassed until the eighteenth century', writes R. J. Forbes with some pardonable exaggeration. But when the Roman Empire at last fell, like a mastodon grown too heavy for its legs to support, Western Europe relapsed into a state of lethargy and dirt. Technology was stagnant for centuries, except in a very few instances, such as the casting of bronze church bells, which were common in the ninth century. 'That peculiar creation of the mediaeval age', Froude called them.

There was a revival in the eleventh century. It was not due to any particular inventiveness in Western Europe but rather to the easier passage of new learning and techniques from the East. Even so, a citizen of Ancient Rome arriving in England at the end of the fourteenth century, after 1000 years of sleep, would have found little in the way of technology to wonder at, and much to condemn.

The period ends with the appearance on the scene of that astonishing genius Leonardo da Vinci at the time when what Carlyle, in the middle of the nineteenth century, called 'the three great elements of modern civilization—Gunpowder, Printing and the Protestant Religion' had begun to exert their influence.

One reads of the details of these changes with absorbing interest in the volume before us. It is beautifully illustrated and produced. And one closes it, temporarily, with a feeling of gratitude to the editors and authors, and to the great Company which has made the work possible.   H. T. TIZARD

Short notices of books

(These notices are descriptive rather than critical and are designed to give a general indication of the nature and scope of the books.)

The Uniqueness of the Individual, by P. B. Medawar. Pp. 191. Methuen & Co. Ltd., London. 1957. 18s. net.

This book is a collection of ten essays on major problems of biology written by Professor P. B. Medawar during the decade 1946–56. It takes its title from the last of these essays, which was written specially for the book. They deal in the main with problems of evolution. The earlier essays have been somewhat revised and annotated to take note of new ideas and to correct errors.

The Analysis of Engineering Structures (third edition), by A. J. S. Pippard and J. F. Baker. Pp. xii + 564. Edward Arnold (Publishers) Ltd., London. 1957. 60s. net.

The purpose of this well-established book is to offer students of engineering a general outline of the theories on which the design of structure is based. A substantial part of the book has been rewritten since the last edition (1943), and some material now readily available elsewhere has been omitted. Arches, rings, and bow-girders are now differently treated, by the more elegant method of super-position. An important revision is that of the chapter on retaining walls, which has been rewritten by Dr A. W. Bishop.

Colorimetric Analysis (second edition), Vol. I, by Noel L. Allport and J. W. Keyser. Pp. xi + 424. Chapman and Hall Ltd., London. 1957. 50s. net.

This is a completely new version of N. L. Allport's 'Colorimetric Analysis', originally published as a single volume in 1945. Since that time the methods and applications of colorimetric analysis have so greatly extended as to make it necessary to publish the new edition in two volumes under joint authorship. This first volume deals with the use of colorimetry in biochemical and clinical analysis: the second volume will deal with metals, foods, pharmaceutical products, and so on. As in the original edition, there is no theoretical discussion. The methods described are critically assessed and their limitations are emphasized.

Physics of Fully Ionized Gases, by Lyman Spitzer. Pp. ix + 105. Interscience Publishers Inc., New York; Interscience Publishers Ltd., London. 1956. Paper covers $1.75; bound, $3.50 net.

Although completely ionized gases are encountered only in exceptional circumstances, those containing an almost negligible proportion of neutral atoms are of considerable practical as well as theoretical interest. For example, in the Sun and the solar corona helium exists mostly as nuclei stripped of the two orbital electrons. This account of the theory of gases consisting wholly of nuclei and electrons is intended for students who have some knowledge of theoretical physics but have made no special study of the kinetic theory of gases.

Ciba Foundation Colloquia on Ageing. Vol. III, Methodology of the Study of Ageing, edited by G. E. W. Wolstenholme and Cecilia M. O'Connor. Pp. x + 202. J. and A. Churchill Ltd., London. 1957. 32s. 6d. net.

This discussion, the third within the field of gerontology to be organized by the Ciba Foundation, was prompted by the fact that a number of long-term experiments are in hand to study the changes with age that occur in man and certain animals. In such experiments proper methodology is of the first importance. This volume contains thirteen papers on gerontological methods presented at the colloquium, together with the discussion that followed.

American Institute of Physics Handbook, edited by Dwight E. Gray. Pp. xi + 1523. McGraw-Hill Book Co. Inc., New York; McGraw-Hill Publishing Co. Ltd., London. 1957. £5 12s. 6d. net.

This is a highly concentrated collection, by ninety specialists, of up-to-date and well-documented physical tables, graphs, and formulae. There are eight sections: on mathematics, mechanics, heat, sound, electricity and magnetism, optics, atomic and molecular physics, and nuclear physics. The last two sections occupy about one-third of the book. The subjects are liberally interpreted: data will be found, for example, relating to such

diverse fields as geodesy, oceanography, radio-astronomy, and aerodynamics.

The Encyclopedia of Chemistry, edited by G. L. Clark and G. G. Hawley. Pp. xvi + 1037. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1957. 156s. net.

This is a collection of articles on pure and applied chemistry. It is written by some five hundred different American experts, and the emphasis is upon American practice. Cross references and an index give some assistance in finding information on topics not given a specific heading.

The First One Hundred and Fifty Years. Pp. xxv + 242. John Wiley & Sons Inc., New York. 1957.

The story of John Wiley & Sons, the scientific publishers, has been written to mark the 150th anniversary of the firm's foundation. It is of interest not merely because of its account of the evolution of a small general publisher into a leading firm in the highly specialized business of scientific publishing, but because it incidentally throws interesting sidelights upon certain aspects of American history since 1807. Handsomely produced, this book is a fitting commemoration of a century and a half of notable achievement.

Statistical Methods in Research and Production, with Special Reference to the Chemical Industry (third edition), edited by Owen L. Davies. Pp. x + 396. Published for Imperial Chemical Industries Ltd. by Oliver and Boyd, Edinburgh. 1957. 45s. net.

This standard handbook of statistical methods for scientific and industrial research workers has been substantially revised since the last (1954) edition. Seven of the eleven chapters have been completely rewritten. Subjects introduced for the first time include the economics of testing and experimentation; sequential sampling; the analysis of covariance; and the estimation of variance components and confidence limits. In the new treatment reliance is placed more on confidence limits than on tests of significance.

Notes on contributors

R. E. RICHARDS,
M.A., D.Phil.,

Was born in 1922 and educated at Colyton Grammar School, Devon, and St John's College, Oxford. From 1944 until 1947 he worked on infra-red spectroscopy in the Physical Chemistry Laboratory at Oxford and in 1948 was elected Senior Demy, Magdalen College. Shortly afterwards he succeeded N. V. Sidgwick as Fellow of Lincoln College. He has since worked on the physical properties of clathrate compounds, and during the past eight years has been exploring the chemical applications of nuclear magnetic resonance, upon which he has published numerous papers. He was awarded the Corday-Morgan Medal of The Chemical Society for 1954, and held a Research Fellowship at Harvard University in 1955.

R. N. ROBERTSON,
B.Sc., Ph.D., F.A.A.,

Was born in Melbourne in 1913 and was educated at St Andrew's College, New Zealand, and the University of Sydney, where he became Linnean Macleay Research Fellow in plant physiology. In 1936 he came to Cambridge for three years to continue his studies with an 1851 studentship. He returned to Sydney in 1939 as assistant lecturer in botany, later becoming lecturer. In 1946 he joined the Commonwealth Scientific and Industrial Research Organisation, and is now chief research officer in the Division of Food Preservation and Transport. His research has been mainly concerned with the movement and accumulation of salts in plants; mitochondria; and the physiology of fruit development and ripening.

CYRIL STANLEY SMITH,
D.Sc.,

Was born in Birmingham in 1903. He was educated at Bishop Vesey's Grammar School, the University of Birmingham, and, after emigrating to the United States in 1924, the Massachusetts Institute of Technology. He spent fifteen years as research metallurgist with the American Brass Company, and during the war he directed the work in metallurgy at the Los Alamos Laboratory. In 1946 he was appointed the first director of the Institute for the Study of Metals of the University of Chicago, a post which he has recently resigned in order to devote more time to laboratory work. He remains professor of metallurgy in the Institute. He has been awarded the U.S. Medal for Merit, and medals of the Franklin Institute and the American Institute of Mechanical Engineers. His research has been in the fields of the constitution and structure of alloys, the metallurgy of plutonium, and the role of surface energy in determining the shape of microconstituents in alloys. On leave from the University in 1955–56, he lived in London and devoted himself to research on the history of science and technology, in which he had long been interested.

E. F. WARBURG,
M.A., Ph.D.,

Was born in 1908 and was educated at Marlborough College and Trinity College, Cambridge. Formerly a Fellow of Trinity College, Cambridge, he is now Curator of the Druce Herbarium, Oxford University. He has worked mainly on the taxonomy of British plants and is joint author of the 'Flora of the British Isles'. He is editor of *Watsonia*, the Journal of the Botanical Society of the British Isles.

H. GUTFREUND,
Ph.D.,

Was born in Vienna in 1921, and came to England in 1938. Between 1943 and 1956 he was associated with several Cambridge University research units first as a research student, then as Assistant in Research in Colloid Science, and lately as Imperial Chemical Industries Research Fellow. He worked first on the structure and properties of protein molecules in solution and during the last four years on the chemical mechanisms of enzyme reactions. In 1952 he was a Rockefeller Foundation Fellow in J. S. Fruton's laboratory at Yale University and since then has spent several periods as Research Associate at the Sterling Chemistry Laboratory of Yale University. He has recently been appointed to the staff of the National Institute for Research in Dairying, where he will continue his study of enzyme mechanisms.

G. PORTER,
M.A., Ph.D., F.R.I.C.,

Was born in 1920 and was educated at the Universities of Leeds and Cambridge. Following war service as a radar officer, he carried out research in the University of Cambridge, where he developed techniques for the observation and study of unstable chemical species. He was elected a Fellow of Emmanuel College, later becoming a demonstrator, then an assistant director of research in physical chemistry. In 1954 he became assistant director of the British Rayon Research Association and in 1955 he was appointed to the chair of physical chemistry in the University of Sheffield. This year he received the Corday-Morgan Medal of The Chemical Society.

Some books received

(*Note.* Mention of a book on this page does not preclude subsequent review.)

BIOLOGY

Biological Aspects of the Transmission of Disease, *edited by C. Horton-Smith. Pp. viii + 184. Published for the Institute of Biology by Oliver and Boyd, Edinburgh. 1957. 21s. net.*

Cold Spring Harbor Symposia on Quantitative Biology. *Vol. XXI*, Genetic Mechanisms: Structure and Function. *Pp. xviii + 392. The Biological Laboratory, Cold Spring Harbor, New York. 1956. $8 net.*

BOTANY

Progress in the Study of the British Flora. Report of the Conference held in 1956 by The Botanical Society of the British Isles, *edited by J. E. Lousley. Pp. 127. The Botanical Society of the British Isles, British Museum, London. 1957. 20s. net.*

CHEMISTRY

Chemical Process Economics in Practice, *by J. James Hur. Pp. iv + 115. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1957. 32s. net.*

Chimica Analitica degli Alimenti, *Vol. II, by Giulio Buogo. Pp. 497. Casa Editrice Ceschina, Milan. 1956. Lire 4500 net.*

La chimie nucléaire et ses applications, *by M. Haïssinsky. Pp. vi + 651. Masson et Cie, Paris. 1957. Paper covers, Fcs. 5000; bound, Fcs. 5600 net.*

Chimie organique générale, *by Jean Vène. Pp. 349. Masson et Cie, Paris. 1957. Paper covers, Fcs. 3500; bound, Fcs. 4100 net.*

Elementary Practical Organic Chemistry. *Pt. I, Small Scale Preparations, by Arthur I. Vogel. Pp. xv + 347 + xiv. Longmans, Green & Co., London. 1957. 21s. net.*

Encyclopedia of Chemical Reactions, *Vol. VI, compiled by C. A. Jacobson and edited by Clifford A. Hampel. Pp. 438. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1956. 100s. net.*

Instrumental Analysis, *by Paul Delahay. Pp. xi + 384. The Macmillan Company, New York and London. 1957. 55s. 6d. net.*

Microchemical Journal, *Vol. I, No. I, edited by Nicholas D. Cheronis and others.*

Pp. 166. Published under the auspices of The Metropolitan Microchemical Society by Interscience Publishers Inc., New York. 1957. Annual subscription $9.60 net.

Organic Synthesis, *Vol. I*, Open-Chain Saturated Compounds; *Vol. II*, Open-Chain Unsaturated Compounds, Alicyclic Compounds, Aromatic Compounds, *by Vartkes Migrdichian. Pp. xxviii + 833 and pp. xiii + 835–1822. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1957. £14 the set.*

Précis des matières colorantes synthétiques. *Vol. II, Matières colorantes, by Henri Wahl. Pp. 398. Presses Universitaires de France, Paris. 1957. Fcs. 2800 net.*

ENGINEERING

Engineering Uses of Rubber, *edited by A. T. McPherson and Alexander Klemin. Pp. 490. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1957. 100s. net.*

Quality Control for Plastics Engineers, *edited by Lawrence M. Debing. Pp. iii + 142. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1957. 40s. net.*

GENERAL SCIENCE

On Human Communication, *by Colin Cherry. Pp. xiv + 333. The Technology Press of Massachusetts Institute of Technology, and John Wiley & Sons Inc., New York; Chapman and Hall Ltd., London. 1957. 54s. net.*

Realities of Space Travel, *edited by L. J. Carter. Pp. 431. Putnam & Co. Ltd., London. 1957. 35s. net.*

Route-Mapping and Position-Locating in Unexplored Regions, *by W. Filchner, E. Przybyllok, and T. Hagen. Pp. 288. Birkhäuser Publishing Co., Basle. 1957. Sw. Fcs. 32 net.*

GEOLOGY

L'évolution de la lithosphère. *Vol. II. Orogenèse, by Henri Termier and Geneviève Termier. Pt. I, pp. 498; Pt. II, pp. 503–940. Masson et Cie, Paris. 1957. Each part: paper covers, Fcs. 9000: bound, Fcs. 9800 net.*

MATHEMATICS

The Fascination of Numbers, *by W. J.*

Reichmann. *Pp. 176. Methuen & Co. Ltd., London. 1957. 15s. net.*

Mathematics and Statistics for use in Pharmacy, Biology and Chemistry, *by L. Saunders and R. Fleming. Pp. x + 257. The Pharmaceutical Press, London. 1957. 27s. 6d. net.*

MEDICINE

British Pharmaceutical Codex 1954, Supplement 1957. *Pp. xiii + 124. The Pharmaceutical Press, London. 1957. 27s. 6d. net.*

Manual of Radiation Therapy, *by K. Wilhelm Stenstrom. Pp. xxx + 94. Charles C. Thomas, Publisher, Springfield, Illinois; Blackwell Scientific Publications, Oxford. 1957. 34s. net.*

The Visual Pigments, *by H. J. A. Dartnall. Pp. vii + 216. Methuen & Co. Ltd., London; John Wiley & Sons Inc., New York. 1957. 30s. net.*

METALLURGY

Chromium, *Vol. II*, Metallurgy of Chromium and its Alloys, *by Marvin J. Udy. Pp. viii + 402. Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London. 1956. 88s. net.*

PHYSICS

The Calculation of Atomic Structures, *by Douglas R. Hartree. Pp. xiii + 181. John Wiley and Sons Inc., New York; Chapman and Hall Ltd., London. 1957. 40s. net.*

The Defect Solid State, *by T. J. Gray, D. P. Detwiler, D. E. Rase, W. G. Lawrence, R. R. West, and T. J. Jennings. Pp. vii + 511. Interscience Publishers Inc., New York; Interscience Publishers Ltd., London. 1957. $11 net.*

The Hypercircle in Mathematical Physics, *by J. L. Synge. Pp. xii + 424. Cambridge University Press, London. 1957. 70s. net.*

Vorlesungen über Atomphysik, *Vol. I, by J. Picht. Pp. viii + 238. Deutscher Verlag der Wissenschaften, Berlin. 1956. DM 18.60 net.*

TECHNOLOGY

Die technischen Anwendungen der Radioaktivität, *by Engelbert Broda and Thomas Schönfeld. Pp. x + 313. Verlag Technik, Berlin. 1956. DM. 19.*